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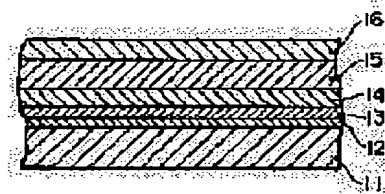
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(54) PIEZOELECTRIC ELEMENT, INK JET TYPE RECORDER HEAD USING THE SAME, INK JET PRINTER AND MANUFACTURE OF PIEZOELECTRIC THIN-FILM ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To eliminate the effects of a remaining strain of a piezoelectric film by specifying the width of the grain boundary of the piezoelectric film, and eliminating the presence of foreign substances after polarizing an element thereof to form a discontinuous layer with the crystal grain boundary which is not continuous to the orientation of adjacent crystal grains.

SOLUTION: None or little foreign substrate exists even after polarizing a piezoelectric film element at the grain boundary of crystals of a piezoelectric film 15, also the grain boundary width is 5 nm or less, it is a discontinuous layer with the crystal grain boundary which is not continuous to the orientation of adjacent crystal grains. Such a structure is suitably attained even in the gel-sol method, utilizing the MOD process for manufacturing the piezoelectric film 15. This manufacturing method is for preparing an inorg. oxide by suppressing the hydrolysis of a metal alkoxide/acetate, using alkanolamine or acetylacetone, etc., and heating and baking a stably dispersed sol.



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CLAIMS

[Claim(s)]

[Claim 1] It is the piezo electric crystal thin film to which the grain boundary where the orientation of this crystal grain does not continue is formed between the crystal grain and crystal grain which constitute said piezo electric crystal thin film, and the foreign matter which deposited from said crystal grain does not exist in this grain boundary mostly in the piezo electric crystal thin film equipped with the piezo electric crystal thin film, and the up electrode arranged on both sides of this piezo electric crystal film and a lower electrode.

[Claim 2] Furthermore, that of said grain boundary is a piezo electric crystal thin film according to claim 1 whose ** is 5nm or less.

[Claim 3] That of this grain boundary is a piezo electric crystal thin film whose ** the grain boundary where the orientation of this crystal grain does not continue is formed between the crystal grain and crystal grain which constitute said piezo electric crystal thin film in the piezo electric crystal thin film equipped with the piezo electric crystal thin film, and the up electrode arranged on both sides of this piezo electric crystal film and a lower electrode, and is 5nm or less further.

[Claim 4] Claim 1 to which said crystal grain constitutes the shape of a column to said vertical electrode, and said grain boundary exists perpendicularly mostly to said vertical electrode thru/or the piezo electric crystal thin film of three given in any 1 term.

[Claim 5] the crystal orientation of said piezo electric crystal thin film — or (111) (100) — it is — claim 1 thru/or the piezo electric crystal thin film of four given in any 1 term.

[Claim 6] For a presentation to be the predetermined compound which consists of a configuration element of said piezo electric crystal thin film, and for this piezo electric crystal thin film demonstrate a piezo-electric operation, said foreign matter is a piezo electric crystal thin film according to claim 1 which is the compound which has a different presentation.

[Claim 7] The allowance content of said foreign matter is a piezo electric crystal thin film according to claim 1 which is what makes a required value an upper limit when attaining that a residual strain does not remain mostly after electric field are impressed to said piezo electric crystal thin film.

[Claim 8] Claim 1 to which an MOD process comes to form said piezo electric crystal thin film thru/or the piezo electric crystal thin film of seven given in any 1 term.

[Claim 9] The piezo electric crystal thin film according to claim 1 or 3 to which the orientation of field bearing of said crystal grain meets mostly the orientation of the polarization shaft of said piezo electric crystal thin film.

[Claim 10] The actuator using said claim 1 thru/or the piezo electric crystal thin film of nine given in any 1 term as a source of mechanical energy.

[Claim 11] The manufacture approach of the piezo electric crystal thin film which is the manufacture approach of the piezo electric crystal thin film equipped with the process which arranges an up electrode and a lower electrode on both sides of the piezo electric crystal thin film which consists of the polycrystalline substance, performs said piezo electric crystal film formation process according to an MOD process, and is characterized by obtaining a piezo electric crystal thin film according to claim 1 or 3 by this.

[Claim 12] The ink jet type recording head which equipped any 1 term of claim 1 thru/or claim 9 with the piezo electric crystal thin film of a publication as a trembler.

[Claim 13] While closing the substrate with which the ink room was formed, and one side of the ink room concerned While closing the field of the diaphragm with which the piezo electric crystal thin film in flexurally oscillating mode was fixed to the front face, and another side of said ink room The ink jet type recording head to which it is the ink jet type recording head which comes to have the nozzle plate with which nozzle opening for ink regurgitation was formed, and said piezo electric crystal thin film becomes any 1 term of claim 1 thru/or claim 9 from the piezo electric crystal thin film of a publication.

[Claim 14] The ink jet printer equipped with the ink jet recording head according to claim 12 or 13.

[Claim 15] The piezo electric crystal thin film whose residual distortion of said piezo electric crystal thin film is 2.5×10^{-4} or less in the piezo electric crystal thin film equipped with the piezo electric crystal thin film it was made to be distorted by impressing electric field.

[Claim 16] A piezoelectric constant is the piezo electric crystal thin film of 150 or more pC/N according to claim 15.

[Claim 17] The actuator which used the piezo electric crystal thin film according to claim 15 or 16 as a vibration source.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a piezo electric crystal thin film and its manufacture approach. This invention relates to the ink jet printer using the ink jet recording head and this which used this piezo electric crystal component further. In detail, this invention relates to amelioration of the new piezo electric crystal thin film which reduced the residual strain as much as possible.

[0002]

[Description of the Prior Art] The actuator using a piezo electric crystal thin film transforms electric energy into mechanical energy, or performs the reverse, and is used for a pressure sensor, a temperature sensor, an ink jet type recording head, etc. In this ink jet type recording head, the piezo electric crystal thin film is used as vibrator used as the driving source of the ink regurgitation.

[0003] This piezo electric crystal thin film has the structure generally equipped with the piezo electric crystal thin film which consists of the polycrystalline substance, and the up electrode and lower electrode which are arranged on both sides of this piezo electric crystal thin film. Generally the presentation of this piezo electric crystal thin film is made into the binary system which uses titanate-acid lead zirconate (henceforth "PZT") as a principal component, or the three-component system which added the third component to PZT of this binary system.

[0004] The piezo electric crystal thin film of these presentations is formed by a spatter, the sol gel process, the MOD process (Metal organic decomposition process), the laser ablation method, a CVD method, etc. The ferroelectric using binary system PZT as these examples is indicated by "Applied Physics Letters, 1991, Vol.58, No.11, and pages 1161-1163." Moreover, JP,6-40035,A and the piezo electric crystal which used binary system PZT for "Journal of The American Ceramic Society, 1973, Vol.56, No.2, and pages 91-96" are indicated.

[0005] When applying a piezo electric crystal thin film to for example, an ink jet type recording head, the piezo electric crystal thin film (PZT film) equipped with 0.4 micrometers - about 20 micrometers thickness is suitable. Since a high piezoelectric strain constant is required of this piezo electric crystal thin film, it heat-treats at the temperature of 700 degrees C or more, and it is usually supposed that it is required to grow up the crystal grain of this piezo electric crystal thin film.

[0006]

[Problem(s) to be Solved by the Invention] When forming the piezo electric crystal thin film (PZT film) equipped with thickness 0.5 micrometers or more and it heat-treats in order to obtain a high piezoelectric strain constant, the problem that a crack occurs is in the film.

[0007] Moreover, the approach of thickening thickness of a piezo electric crystal thin film by applying a sol or a gel constituent, calcinating at an elevated temperature, crystallizing a piezo electric crystal thin film, and repeating this is "Philips J.Res.47 (1993') pages 263-285". It is indicated.

[0008] The piezo electric crystal thin film obtained by this approach has the problem that workability is bad while it has a layer-like laminating interface and cannot acquire a good piezo-

electric property. Moreover, if it heat-treats repeatedly, it will lead also to degradation of piezo-electric properties, like a crystal becomes non-orientation.

[0009] Here, although a piezo electric crystal thin film is usually formed on the lower electrode formed on the substrate, the problem that curvature and a strain arise is in a substrate by heat treatment performed in case this piezo electric crystal thin film is formed. Moreover, it is also required between a lower electrode and a piezo electric crystal thin film to acquire good adhesion.

[0010] Then, in order to raise the piezo-electric distorted constant of a piezo electric crystal thin film, when this invention persons examined many things, it found out that it was effective that the crystal of a piezo electric crystal thin film is predetermined crystal orientation, and have a columnar structure, and particle size has further the crystal structure which are 0.1 micrometers thru/or 0.5 micrometers (Japanese Patent Application No. No. 288757 [nine to]).

[0011] However, when this invention persons inquired further, it came to discover the following problems. When electric field are impressed to the piezo electric crystal thin film of a virginal state, even if it removes this, a residual strain and a polarization strain occur in a piezo electric crystal thin film, and cannot acquire a good piezo-electric distortion property (variation rate property). That is, if electric field join a piezo electric crystal thin film and polarization of this is carried out, it will move in the domain (crystal grain) of the piezo electric crystal which forms a piezo electric crystal thin film so that a polarization shaft may be set in the direction of electric field. Then, it is thought that a cavity occurs in the grain boundary of particles and this causes a residual strain.

[0012] Then, in order that this invention may solve this technical problem, the effect of the residual strain in a piezo electric crystal thin film can be removed, and it aims at offering the device excellent in the piezo-electric strain property.

[0013]

[Means for Solving the Problem] As a result of this invention person's examining many things about the piezo electric crystal thin film which can attain such an object, it came to find out the piezo electric crystal thin film equipped with the following properties.

[0014] There is [whose foreign matter does not exist in it after carrying out polarization processing (polling) of the piezo electric crystal thin film to the grain boundary which is a boundary of the crystal grain of a piezo electric crystal thin film] little abundance of a foreign matter. Moreover, the width of face of a grain boundary should be 5nm or less. Moreover, the orientation of the crystal grain with which the grain boundary adjoins should be a not continuous discontinuity layer.

[0015] According to this invention person's knowledge, such structure is suitably attained also in a sol gel process by using an MOD process as stated above for manufacture of a piezo electric crystal thin film. Although a foreign matter is a compound formed from the element which constitutes PZT, that in which the presentation differs from PZT is said.

[0016] For example, it is lead oxide (PbO). After impressing electric field to a piezo electric crystal thin film, the abundance of a foreign matter should just be regulated so that the abundance of a foreign matter may become the range of a request of a residual strain. For example, 2.5×10 to four or less are desirable. Or it is the range where improvement in the piezo-electric effect like the after-mentioned is obtained. After polarization processing of the piezo electric crystal thin film with which a foreign matter exists is carried out, it is clear to become the cause of a residual strain by X diffraction analysis mentioned later. In addition, a residual strain means a strain in case field strength is 0 kv/cm.

[0017] Since there is little migration of the domain of the piezo electric crystal thin film produced by electric-field impression at the time of polarization processing of a piezo electric crystal thin film or actuation according to this invention, there is [whether a residual strain is small and] almost nothing. This means that there are few hysteresis properties over electric-field impression for a piezo electric crystal thin film. Consequently, a distortion-electrical-potential-difference (electric field) property is good, and can offer a piezo electric crystal thin film with a big variation rate.

[0018] The piezoelectric constant d_{31} from which an index is served as, the piezo-electric effect, i.e., displacement-voltage characteristic, of a piezo electric crystal thin film of this invention, is 180 or more pc/N, and becomes possible [obtaining the piezoelectric constant of 1.2 times or more]

as compared with the conventional thing.

[0019] When the variation rate of the piezo electric crystal film impresses an electrical potential difference to a piezo electric crystal thin film, it is generated from a gap of the relative position of a metal atom and an oxygen atom. In the grain boundary between domains (between adjacent crystal grain), an opening occurs as a result of migration of a domain. Existence of this opening reduces the withstand voltage of a piezo electric crystal thin film.

[0020] It is checked by this invention person that decreasing a foreign matter makes a residual strain fall. Moreover, in this invention, lessening width of face of the grain boundary in a piezo electric crystal thin film leads to the ability of the grain boundary itself [used as the radical of the opening leading to residual distortion] to be controlled.

[0021] The crystal grain of a piezo electric crystal thin film constitutes the shape of a column to a vertical electrode, and it is desirable that the direction of field bearing of the crystal concerned is field (001) bearing of tetragonal system or field (111) bearing of a rhombohedral system. In addition, it is good also in the field bearing of (100).

[0022] Since crystallization of the piezo electric crystal thin film by the sol gel process or the MOD process takes place from a lower electrode side, when controlling the crystal orientation of a piezo electric crystal thin film, it needs to be devised. For this reason, it is possible to form seed crystal when forming the crystal of a piezo electric crystal thin film on a bottom electrode.

[0023] Seed crystal (source of a crystal) is constituted on the platinum crystal which consists of titanium and constitutes a lower electrode, or its grain boundary. Said piezo electric crystal thin film has the crystal orientation of field bearing as stated above, and is equipped with the column-like particle size of 0.1 micrometers thru/or the 0.5-micrometer crystal structure.

[0024] Furthermore, the crystal of the piezo electric crystal film which grew as a nucleus is suitably formed ranging over two or more crystal grain of a lower electrode in the source of a crystal formed in the grain boundary of a lower electrode. By carrying out like this, the adhesion between a piezo electric crystal thin film and a lower electrode improves.

[0025] Furthermore, other piezo electric crystal thin films of this invention are characterized by becoming more than a value almost equal to the particle size of said lower electrode, or it, when the particle size of said lower electrode is set as a desirable particle size when said piezo electric crystal demonstrates a piezo-electric property, and the particle size of the crystal of said piezo electric crystal grows considering said source of a crystal as a nucleus.

[0026] The ink jet type recording head of this invention is characterized by having a piezo electric crystal thin film as stated above as vibrator. With one operation gestalt, this ink jet type recording head is characterized by coming to have the substrate with which the ink room was formed, the diaphragm with which the piezo electric crystal thin film in flexurally oscillating mode was fixed to the front face while closing one side of the ink room concerned, and the nozzle plate with which nozzle opening for ink regurgitation was formed while closing the field of another side of said ink room, and said piezo electric crystal thin film consisting of a piezo electric crystal thin film as stated above.

[0027] By forming an island-like crystal kind on between [which constitutes a lower electrode] platinum crystal grain, this seed crystal is used as a nucleus, and it grows up in the shape of a column, and has the predetermined field bearing orientation **** crystal structure. When it is going to obtain the orientation of (111), this island-like titanium is not used.

[0028] Furthermore, when the crystal of said lower electrode is set as a desirable particle size when said piezo electric crystal demonstrates a piezo-electric property, and the crystal of said piezo electric crystal grows considering said source of a crystal as a nucleus, the diameter of crystal grain of said piezo electric crystal can be carried out beyond a value almost equal to the particle size of a lower electrode. That is, since the crystal of a piezo electric crystal thin film can have the structure over two or more lower electrode crystals, it becomes possible to have the particle size exceeding the particle size of a lower electrode. Moreover, by forming the source of a crystal in the grain boundary which cannot receive effect in the stacking tendency of a lower electrode crystal easily, the crystal of a piezo electric crystal thin film can grow as a nucleus, can have this source of a crystal, and the stacking tendency of a piezo electric crystal thin film crystal can be made into the target thing.

[0029] Furthermore, this invention is characterized by the residual distortion of said piezo electric crystal thin film being 2.5×10 to four or less in the piezo electric crystal thin film equipped with the piezo electric crystal thin film it was made to be distorted by impressing electric field. A piezoelectric constant is 150 or more pC/N preferably. Furthermore, this invention is characterized by being the actuator which used these piezo electric crystal thin films as a vibration source.

[0030] [Embodiment of the Invention] Next, the gestalt of operation concerning this invention is explained with reference to a drawing. In addition, the gestalt of this operation explains the case where the PZT film is formed as piezo electric crystal film. Drawing 1 is the mimetic diagram showing the configuration of the piezo electric crystal component concerning this invention. As shown in drawing 1, this piezo electric crystal thin film is equipped with the up electrode 16 formed on a silicon substrate 11, the silicon oxide 12 formed on the silicon substrate 11, the lower electrode 14 formed on silicon oxide the titanic-acid-ized film (Ti/TiO₂/Ti) 13 formed 12 top and the titanic-acid-ized film 13, the PZT film 15 formed on the lower electrode 14, and the PZT film 15, and is constituted. This titanic-acid-ized film is for improving the adhesion of a lower electrode and a PZT thin film. A vertical electrode consists of platinum, for example, respectively.

[0031] The PZT film 15 consists of the polycrystalline substance, and as the grain boundary of this crystal grain shows drawing 14 and drawing 15, it exists in the direction which extends to the flat surface of the vertical section electrodes 14 and 16 in an abbreviation perpendicular direction and the direction of thickness of a piezo electric crystal thin film. That is, the columnar structure is accomplished like the after-mentioned [the crystal grain of PZT].

[0032] Orientation of the crystal structure of this PZT film 15 is mainly carried out to the crystal face of which field bearing as stated above.

[0033] here — “the amount of preferred orientation” — for example, the wide angle XRD — when the reflectivity of the field bearing (XYZ) side of the PZT film is expressed with $I(XYZ)$ by law, it is defined as being what is expressed as $I(XYZ)/[I(100) + I(110) + I(111)]$.

[0034] That to which this PZT film 15 uses binary system as a principal component, and the thing which uses as a principal component three-component system which added the third component to this binary system are used suitably. What has the presentation expressed with the chemical formula of $Pb(Zr_xTi_{1-x})O_3 + YPbO$ (being here $0.40 \leq x \leq 0.6$, $0 \leq Y \leq 0.3$) as a desirable example of binary system PZT is mentioned.

[0035] Moreover, as a desirable example of three-component system PZT, what has the presentation expressed with the chemical formula shown in the following which added the third component is mentioned to PZT of said binary system.

[0036] $PbTi_aZr_b(AgBh)_cO_3 + ePbO + (fMgO)_n$ (here, A expresses the trivalent metal chosen from the group which consists of a divalent metal chosen from the group which consists of Mg, Co, Zn, Cd, Mn, and nickel, or Sb, Y, Fe, Sc, Yb, Lu, In and Cr.) Moreover, B expresses the pentavalent metal chosen from the group which consists of Nb, Ta, and Sb, or the metal of 6 ** chosen from the group which consists of W and Te. Moreover, although it is $a+b+c=1$, $0.35 \leq a \leq 0.55$, $0.25 \leq b \leq 0.55$, $0.1 \leq c \leq 0.4$, $0 \leq e \leq 0.3$, $0 \leq f \leq 0.15$, $g=f=1/2$, and $n=0$ however, A — a trivalent metal — it is — and B — the metal of 6 ** — not but — moreover, the case where g is $1/3$, and h is $2/3$, and Mg and B of A are Nb(s) when A is a divalent metal and B is a pentavalent metal — as long as — n expresses 1. As a more desirable example of three-component system, magnesium lead niobate, i.e., A, is Mg, B is Nb, and that $1/$ whose $3h$ g is $2/3$ is mentioned.

[0037] Furthermore, even if it is any of these binary system PZT and three-component system PZT, in order to improve the piezo-electric property, Ba, Sr, La, Nd, Nb, Ta, Sb, Bi, W, Mo, calcium, etc. of a minute amount may be added. In three-component system, addition of Sr not more than 0.10 mol % and Ba is especially much more desirable to an improvement of a piezo-electric property. Moreover, since addition of Mn not more than 0.10 mol % and nickel improves the degree of sintering in three-component system, it is desirable.

[0038] Next, the manufacture approach of the piezo electric crystal thin film equipped with this structure is explained with reference to a drawing. Drawing 2 (a) thru/or drawing 2 (c) are the sectional views showing the production process of the piezo electric crystal thin film mentioned above. At the process shown in drawing 2 (a), it oxidizes thermally to a silicon substrate 11, and

the silicon oxide 12 whose thickness is about 0.3–1.2 micrometers is formed on a silicon substrate 11. Next, thickness forms the titanate-acid-ized film 13 which is 0.01 micrometers thru/or about 0.04 micrometers on silicon oxide 12 by the sputter. Subsequently, the diameter of crystal grain forms the lower electrode 14 which consists of platinum by 0.01 thru/or 0.3 micrometers on the titanate-acid-ized film 13 by the sputter at about 0.2–0.8-micrometer thickness.

[0039] Next, at the process shown in drawing 2 (b), titanium is formed in the shape of an island by the sputter on the lower electrode 14 formed at the process shown in drawing 2 (a). Island-like titanium can be formed by making this titanium into 40 thru/or 60Å thickness.

[0040] the crystal structure of the piezo electric crystal thin film which grew considering this titanium as a source of a crystal — or (001) (100) it has the orientation to a field and crystal grain is set to 0.1 micrometers thru/or 0.5 micrometers. In making crystal system of a PZT thin film into a rhombohedral system (111), it does not use the process which forms island-like titanium.

[0041] This manufacture approach is an approach of carrying out heating baking of a metal alkoxide and the sol which controlled hydrolysis of acetate and carried out stable distribution using alkanolamine or an acetylacetone, and adjusting an inorganic oxide. This manufacture approach consists of each following process.

[0042] a. In the gestalt of membrane formation process book operation of a sol constituent, the constituent for PZT thin film fabrication can distribute the metal alkoxide or the acetate which can form the PZT film which is the metal component of the sol for constituting the PZT film among the 2-n-butoxy ethanol as for example, a main solvent, and can be adjusted. At this time, 2 and 2' imino BIETA Norian (an alkoxide or hydrolysis inhibitor to acetate) is simultaneously put in into a solution.

[0043] In this invention, the presentation of the PZT film mentioned above can be acquired by controlling the presentation of the metal in a sol. That is, let titanium, a zirconium, lead, the alkoxide of each metal component of further others, or acetate be a start raw material.

[0044] Here, there is an advantage that the presentation of the metal component which will constitute the PZT film by the time it considers as the PZT film (piezo electric crystal thin film) eventually is maintained mostly. That is, the presentation of a metal component [in / there are very little metal component and fluctuation especially according to evaporation of a lead component etc. during baking and annealing treatment, therefore / these start raw materials] will be in agreement with the metal presentation in the PZT film obtained eventually. That is, the presentation of a sol is determined according to the piezo electric crystal film (the gestalt of this operation PZT film) which it is going to generate.

[0045] Moreover, in order to obtain the PZT film which does not have lack of a lead component by evaporation of the lead component mentioned above with the gestalt of this operation, 15-mol the thing carried out to an excess to % is preferably more desirable than the amount of which a lead component is required from a stoichiometry in a sol to 20-mol %.

[0046] As for this sol, with the gestalt of this operation, it is desirable to be used as a constituent mixed with the organic high molecular compound. This organic high molecular compound prevents effectively that absorb the residual stress of a thin film at the time of desiccation and baking, and a crack arises in this thin film. If the gel containing this organic macromolecule is specifically used, pore will arise in the gelled thin film which is mentioned later. It is thought that this pore absorbs the residual stress of a thin film in pre annealing and the annealing process which are mentioned further later.

[0047] Here, as an organic high molecular compound used preferably, polyvinyl acetate, hydroxypropylcellulose, a polyethylene glycol, the polyethylene-glycol monomethyl ether, a polypropylene glycol, polyvinyl alcohol, polyacrylic acid, a polyamide, polyamic acid, an acetyl cellulose, its derivative, and those copolymers are mentioned.

[0048] In addition, with the gestalt of this operation, the porosity gel thin film which is 1 micrometer or less in magnitude, and had large distribution can be formed by adding a hydroxy pro PUROI cellulose for the porosity gel thin film which has much about 0.05-micrometer pores by adding polyvinyl acetate.

[0049] With the gestalt of this operation, a with an average molecular weight of about 285 to 800 thing is suitably used as a polyethylene glycol. Moreover, as a polypropylene glycol, a with an

average molecular weight of about 300 to 800 thing is used suitably.

[0050] By the manufacture approach concerning the gestalt of this operation, this sol constituent is first applied on the lower electrode 14 (refer to drawing 2 (b)) which is going to form the PZT film 15. Especially the method of application at this time is not limited, but the approach usually performed, for example, a spin coat, (1500 revolutions per minute), a DIP coat, a roll coat, a bar coat, etc. can perform it. Moreover, it can also apply by flexographic printing, screen-stencil, offset printing, etc.

[0051] Moreover, when the process after it is taken into consideration, as for the thickness of the film per [which is formed of said spreading] layer, it is desirable to control so that the thickness of the porosity gel thin film formed in the gelation process mentioned later is set to 0.1 thru/or 0.3 micrometers, and it is good to be more preferably referred to as about 0.15 micrometers.

[0052] Next, the applied sol constituent is heated at air drying or the temperature (for example, 180-degree Centigrade 10 minutes) of 200 degrees C or less. Here, said sol constituent can be further applied on this film dried (heating), and thickness can also be thickened. In this case, as for the film used as a substrate, it is desirable to dry at the temperature of 80 degrees C or more.

[0053] b. Calcinate the film obtained at the gelation process of the film which consists of a sol constituent, next the membrane formation process of a sol constituent mentioned above, and form the porosity gel thin film which consists of an amorphous metallic oxide which does not contain the residual organic substance substantially. Baking is sufficient temperature to gel the film of a sol constituent and remove the organic substance out of the film, and is performed by [sufficient] carrying out time amount heating.

[0054] It is desirable to make burning temperature into 300–500 degrees C with the gestalt of this operation, and it is still more desirable to make it 380–420 degrees C. Although it changes with temperature and the formats of a furnace to be used, when a cleaning furnace is used for example, about 10 – 120 minutes of firing time are desirable, and it is more desirable to consider as about 15 – 60 minutes. Moreover, when a hot plate is used, about 1 – 60 minutes is desirable, and it is still more desirable to consider as about 5 – 30 minutes. Of the above process, a porosity gel thin film is formed on the lower electrode 14.

[0055] c. Carry out heating baking of the porosity gel thin film obtained at the pre annealing process, next the process b mentioned above, and change this film into the film which consists of a metal oxide film of a crystalline substance. What is necessary is not to perform baking until a perovskite mold crystal occupies most during a crystal, and just to terminate it, when a gel thin film crystallizes to homogeneity although carried out at temperature required in order to change a porosity gel thin film into the film which consists of a metallic oxide of a crystalline substance. With the gestalt of this operation, as a burning temperature, the range of 500–800 degrees C is desirable, and it is more desirable to calcinate in the range which is 550–750 degrees C. Although it changes with burning temperature and the formats of a furnace to be used, when using an annealing furnace, for example, about 0.1 – 5 hours of firing time are desirable, and it is more desirable. [of about 0.5 – 2 hours] Moreover, when a RTA (Rapid Thermal Annealing) furnace is used, about 0.1 – 10 minutes is desirable, and about 1 – 5 minutes is more desirable. Here, in RTA, heating for 1 minute was performed Centigrade 600-degree 5-minute + Centigrade 725 degrees in an oxygen ambient atmosphere.

[0056] Moreover, with the gestalt of this operation, this pre annealing process can be divided into two steps, and can be carried out. As a first stage story, annealing can be performed at the temperature of the range of 500–600 degrees C, next, specifically, annealing can be first performed at the temperature of the range of 600–800 degrees C as a second stage story. Furthermore, as a first stage story, annealing can be performed at the temperature of the range of 500–550 degrees C, next annealing can be preferably performed at the temperature of the range of 600–750 degrees C as a second stage story. According to this process, the porosity gel thin film was transformed to the film which consists of a metal oxide film of a crystalline substance.

[0057] d. Change into the film which consists of a metal oxide film according to the pre annealing process of Process C after repeating the processes a and b mentioned above further 3 times a repeat process, next henceforth and carrying out the four-layer laminating of the polycrystal gel thin film.

[0058] In ranking second or (100) (001) forming the piezo electric crystal thin film of orientation, titanium is formed in the shape of an island by the approach as stated above on PZT, and it repeats the processes a, b, and c as stated above further 4 times.

[0059] What is necessary is just to determine suitably the number of laminatings of the cascade screen obtained as a result of this repeat process in consideration of the thickness of the final PZT film 15. Here, it is good that it is 0.15 micrometers of hits much more. In addition, it cannot be overemphasized that it is desirable that it is the thickness which a crack etc. does not generate in degree process (process e) mentioned later.

[0060] At this repeat process, the porosity gel thin film which newly formed the porosity gel thin film and was newly formed on the film formed previously as a result of subsequent pre annealing turns into film formed previously and film unified substantially.

[0061] Here, a discontinuity layer may be not only when there is no discontinuity layer between the layers by which the laminating was carried out to the film unified substantially but between the layers by which the laminating was carried out unlike the case of the PZT film 15 concerning the gestalt of this operation obtained eventually. And in repeating Processes a and b further, a still newer porosity gel thin film is formed, and this new porosity gel thin film turns into film substantially united with the cascade screen of the crystalline substance obtained above as a result of subsequent pre annealing.

[0062] e. Perovskite mold crystal growth process (final annealing)

Next, annealing is performed on the film obtained at said process d in 800–1000 degrees C still more preferably the burning temperature of 600–1200 degrees C. Although it changes with burning temperature and the formats of a furnace to be used, when an annealing furnace is used for example, about 0.1 – 5 hours of firing time are desirable, and it is more desirable. [of about 0.5 – 2 hours] Moreover, when a RTA furnace is used, about 0.1 – 10 minutes is desirable, and about 0.5 – 3 minutes is more desirable. Here, it set [aforementioned] RTA and this process was performed in 1 minute and 650–degree Centigrade oxygen [5 +900 degree] ambient atmosphere per minute.

[0063] Moreover, with the gestalt of this operation, it can perform dividing this perovskite mold crystal growth process, i.e., annealing, into two steps, and carrying it out. Annealing is performed at the temperature of about 600–800 degrees C, and, specifically, the temperature of 800–1000 degrees C performs annealing on a second stage story on a first stage story. Furthermore, preferably, annealing can be performed at the temperature of about 600–750 degrees C, and the temperature of 800–950 degrees C can perform annealing on a second stage story on a first stage story.

[0064] Of the above actuation, PZT whose thickness the particle size which consists of the column-like polycrystalline substance is 1.2 micrometers in 0.1 micrometers thru/or 0.5 micrometers is formed on the lower electrode 14. Here, the effectiveness which titanium gives about crystallization of PZT is explained. This effectiveness is checked by this invention person using the electron microscope.

[0065] In drawing 1 , island-like titanium is formed of the spatter on the grain boundary of the lower electrode 14. The diameters of crystal grain of a lower electrode are 0.01 thru/or 0.3 micrometers. Since the platinum of using a lower electrode as a columnar crystal with such a diameter of crystal grain is FCC structure, it is easy to become a columnar crystal, and the diameter of crystal grain is possible from the reason for being controllable by the membrane formation rate at the time of a spatter.

[0066] If it is going to form an island-like titanium crystal in the front face of a lower electrode, it will become the inclination for the island-like crystal of titanium to be formed in the grain boundary during the low platinum crystal of the surface energy of platinum. At this time, ranging over two or more titanium crystals, the PZT crystal grain which grows considering titanium as a nucleus reaches, and is formed.

[0067] Drawing 3 is a mimetic diagram in which it is shown like the formation fault of the PZT crystal checked by the electron microscope, (1) is drawing which met in the height direction of a PZT crystal, and (2) is drawing which met in the direction of a path (width of face) of a PZT crystal. Drawing 4 is a actual electron microscope photograph, and the crystal of column-like PZT is formed on Pt electrode. Titanium crystal 14A is formed in the grain boundary of the lower

electrode crystal 14.

[0068] If PZT is grown up by using a titanium crystal as a nucleus, the crystal grain will grow so that PZT may straddle two or more platinum crystals of an adjoining lower electrode. Usually, its orientation of 111 is stable, and although production is also easy, if Pt forms the seed crystal of titanium in the grain boundary which cannot be more easily influenced of the orientation of platinum, it can use the crystal of PZT as the columnar crystal of a direction (001) which is not influenced of crystal-face bearing of platinum (100). Furthermore, since the crystal grain of PZT is formed ranging over two or more lower electrodes, it is expected that adhesion with a lower electrode will improve more.

[0069] It is chart drawing of an X-ray diffraction analysis (XRD) when drawing 5 forms the piezo electric crystal thin film PZT on the lower electrode in which island-like titanium was formed, and drawing 6 is chart drawing when not forming island-like titanium. If drawing 5 is mutually compared with drawing 6, when not forming island-like titanium, orientation (111) becomes strong and the piezo electric crystal constant of the orientation of the PZT film is also 180 pC/N. On the other hand, when island-like titanium is formed, or it is PZT (001) (100), when orientation becomes strong and the rate also increases to orientation (111), a piezoelectric constant also becomes high with 190 pC/N. Here, a piezoelectric constant is that for which it asked from the displacement (distortion)-voltage characteristic, and the piezo-electric effect at the time of impression electric-field 250 kv/cm is shown.

[0070] Furthermore, titanium forms in the shape of an island, and three-layer sequential formation of the PZT layer in which titanium was formed in the shape of an island is carried out, and further, if what carried out four-layer sequential formation of the PZT further is crystallized, titanium is used as a nucleus, and PZT will crystalize like previous statement and it will crystalize according to the diameter of crystal grain and the crystal structure of PZT which other PZT(s) adjoin. The island-like titanium between a PZT layer and a PZT layer is also controlled like previous statement of crystallization of PZT on titanium.

[0071] In addition, it asked for measurement of a piezoelectric strain constant from the distortion-voltage characteristic of the cantilever shown in drawing 9 and drawing 10. That is, a piezoelectric constant (d_{31}) is computed from Δ measured since displacement Δ was obtained by the degree type and thickness [of Si substrate] H , Young's modulus Y_{Si} and Poisson's ratio ν , Young's modulus Y_{PZT} of the piezo electric crystal film and the free length L of a cantilever, and applied voltage V .

[0072]

$\Delta = d_{31} \cdot V$, and $(Y_{PZT}/Y_{Si}) \cdot (3L^2/H^2) \cdot (1-\nu_{Si}) / (1-\nu_{PZT})$ The following relation between epsilon and displacement Δ is about distortion, and distortion epsilon can be calculated again.

[0073] t is the thickness of a piezo electric crystal thin film.

[0074] $\epsilon = \{H^2 / (3(1-\nu_{Si}) \cdot t \cdot L^2)\} \cdot \Delta$ drawing 7 shows the transmission electron microscope image of the piezo electric crystal thin film obtained here. When this invention person examined the grain boundary (grain boundary) between two adjoining crystals (grain1 and grain2), it was about 5nm or less. There were some which cannot observe the grain boundary mostly. On the other hand, the transparency mold microscope image of the piezo electric crystal thin film created as an example of a comparison of this invention is shown in drawing 8. The film as this example of a comparison added ten-mol superfluous water to one mol of PZT(s) into the sol first, accelerated hydrolysis beyond the need, and it performed at 650 degrees C for 5 minutes, 1 minute performed final annealing temperature at 700 degrees C, and it created it. When this invention person measured the grain boundary of this thing, it had width of face of 7-12nm or more.

[0075] Furthermore, the residual strain to electric-field impression with the piezo electric crystal thin film obtained according to this operation gestalt was measured by making the piezo electric crystal thin film of drawing 8 into the example of a comparison.

[0076] Drawing 9 and drawing 10 are property drawings showing the measurement result when measuring on the conditions of fixing temperature for both residual strain and carrying out increment reduction of the electric field gradually. Drawing 9 is property drawing of the example of a comparison. On the other hand, although drawing 10 was created according to the MOD process, it is a result. as for it, the result of the latter turns out that it is markedly alike compared with the

former, and the residual strain is decreasing. When a residual strain falls, the piezo-electric property of the piezo electric crystal thin film of this invention becomes more than d_{31} , and becomes possible [demonstrating one about 1.2 times the piezo-electric strain property of this as compared with the conventional thing]. Measurement of a residual strain was performed using the cantilever. Initial displacement in case an electrical potential difference is zero is equivalent to a residual strain. In the piezo electric crystal thin film with which crystal grain is assembled in the pillar-shaped direction, i.e., a grain boundary, by the thing of bulk with the random direction of a grain boundary of crystal grain, a residual strain becomes large to an almost right-angled thing to a vertical electrode.

[0077] Furthermore, the trial to the foreign matter in the grain boundary of the piezo electric crystal thin film obtained by this example was performed. This trial was based on the electron ray diffraction pattern obtained according to the conditions of limit visual field diffraction. The white dot shown in drawing 11 and drawing 12 is a PZT crystal. The part shown by drawing 11 and drawing 12 is a part equivalent to the PZT grain boundary, and a PZT crystal presentation is a part for the foreign matter of the presentation from which the part surrounded by ** in this part differs. Drawing 11 is a pattern concerning the example of a comparison, and drawing 12 is a pattern concerning this operation gestalt. The pattern of drawing 12 is understood that there is little abundance of an impurity clearly as compared with the pattern of drawing 11 .

[0078] If it returns and explains to drawing 1 , after ending the process of drawing 2 (b), it will shift to the process shown in (c). At this process, thickness forms the up electrode 16 which consists of about 0.05–0.2–micrometer platinum by the spatter on the PZT film 15 obtained at the process shown in (b).

[0079] Thus, the piezo electric crystal thin film as shown in drawing 1 was obtained. In addition, it was checked that the surface of discontinuity of the shape of a layer by the laminating which there is no generating of a crack and was mentioned above in the cross section does not exist in the obtained PZT film 15, either.

[0080] Drawing 13 is the sectional view showing one ink reservoir part of the ink jet type recording head which used the piezo electric crystal thin film concerning this invention as a trembler.

[0081] The ink jet type recording head concerning the gestalt 3 of operation The silicon substrate 21 in which the ink reservoir 27 was formed as shown in drawing 13 , The diaphragm 22 formed on the silicon substrate 21, and the lower electrode 23 formed in the request location on a diaphragm 22,

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TECHNICAL FIELD

[Field of the Invention] This invention relates to a piezo electric crystal thin film and its manufacture approach. This invention relates to the ink jet printer using the ink jet recording head and this which used this piezo electric crystal component further. In detail, this invention relates to amelioration of the new piezo electric crystal thin film which reduced the residual strain as much as possible.

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PRIOR ART

[Description of the Prior Art] The actuator using a piezo electric crystal thin film transforms electric energy into mechanical energy, or performs the reverse, and is used for a pressure sensor, a temperature sensor, an ink jet type recording head, etc. In this ink jet type recording head, the piezo electric crystal thin film is used as vibrator used as the driving source of the ink regurgitation.

[0003] This piezo electric crystal thin film has the structure generally equipped with the piezo electric crystal thin film which consists of the polycrystalline substance, and the up electrode and lower electrode which are arranged on both sides of this piezo electric crystal thin film. Generally the presentation of this piezo electric crystal thin film is made into the binary system which uses titanate-acid lead zirconate (henceforth "PZT") as a principal component, or the three-component system which added the third component to PZT of this binary system.

[0004] The piezo electric crystal thin film of these presentations is formed by a sputter, the sol gel process, the MOD process (Metal organic decomposition process), the laser ablation method, a CVD method, etc. The ferroelectric using binary system PZT as these examples is indicated by "Applied Physics Letters, 1991, Vol.58, No.11, and pages 1161-1163." Moreover, JP,6-40035,A and the piezo electric crystal which used binary system PZT for "Journal of The American Ceramic Society, 1973, Vol.56, No.2, and pages 91-96" are indicated.

[0005] When applying a piezo electric crystal thin film to for example, an ink jet type recording head, the piezo electric crystal thin film (PZT film) equipped with 0.4 micrometers - about 20 micrometers thickness is suitable. Since a high piezoelectric strain constant is required of this piezo electric crystal thin film, it heat-treats at the temperature of 700 degrees C or more, and it is usually supposed that it is required to grow up the crystal grain of this piezo electric crystal thin film.

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to this invention, there are few residual strains and it is possible to obtain the piezo electric crystal thin film excellent in the piezo-electric strain property. Since this piezo electric crystal thin film can demonstrate the variation rate which was excellent when electric field were impressed, the ink jet recording head equipped with this can enlarge ink discharge quantity.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] When forming the piezo electric crystal thin film (PZT film) equipped with thickness 0.5 micrometers or more and it heat-treats in order to obtain a high piezoelectric strain constant, the problem that a crack occurs is in the film.

[0007] Moreover, the approach of thickening thickness of a piezo electric crystal thin film by applying a sol or a gel constituent, calcinating at an elevated temperature, crystallizing a piezo electric crystal thin film, and repeating this is "Philips J.Res.47 (1993) pages 263-285". It is indicated.

[0008] The piezo electric crystal thin film obtained by this approach has the problem that workability is bad while it has a layer-like laminating interface and cannot acquire a good piezo-electric property. Moreover, if it heat-treats repeatedly, it will lead also to degradation of piezo-electric properties, like a crystal becomes non-orientation.

[0009] Here, although a piezo electric crystal thin film is usually formed on the lower electrode formed on the substrate, the problem that curvature and a strain arise is in a substrate by heat treatment performed in case this piezo electric crystal thin film is formed. Moreover, it is also required between a lower electrode and a piezo electric crystal thin film to acquire good adhesion.

[0010] Then, in order to raise the piezo-electric distorted constant of a piezo electric crystal thin film, when this invention persons examined many things, it found out that it was effective that the crystal of a piezo electric crystal thin film is predetermined crystal orientation, and have a columnar structure, and particle size has further the crystal structure which are 0.1 micrometers thru/or 0.5 micrometers (Japanese Patent Application No. No. 288757 [nine to]).

[0011] However, when this invention persons inquired further, it came to discover the following problems. When electric field are impressed to the piezo electric crystal thin film of a virginal state, even if it removes this, a residual strain and a polarization strain occur in a piezo electric crystal thin film, and cannot acquire a good piezo-electric distortion property (variation rate property). That is, if electric field join a piezo electric crystal thin film and polarization of this is carried out, it will move in the domain (crystal grain) of the piezo electric crystal which forms a piezo electric crystal thin film so that a polarization shaft may be set in the direction of electric field. Then, it is thought that a cavity occurs in the grain boundary of particles and this causes a residual strain.

[0012] Then, in order that this invention may solve this technical problem, the effect of the residual strain in a piezo electric crystal thin film can be removed, and it aims at offering the device excellent in the piezo-electric strain property.

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MEANS

[Means for Solving the Problem] As a result of this invention person's examining many things about the piezo electric crystal thin film which can attain such an object, it came to find out the piezo electric crystal thin film equipped with the following properties.

[0014] There is [whose foreign matter does not exist in it after carrying out polarization processing (polling) of the piezo electric crystal thin film to the grain boundary which is a boundary of the crystal grain of a piezo electric crystal thin film] little abundance of a foreign matter. Moreover, the width of face of a grain boundary should be 5nm or less. Moreover, the orientation of the crystal grain with which the grain boundary adjoins should be a not continuous discontinuity layer.

[0015] According to this invention person's knowledge, such structure is suitably attained also in a sol gel process by using an MOD process as stated above for manufacture of a piezo electric crystal thin film. Although a foreign matter is a compound formed from the element which constitutes PZT, that in which the presentation differs from PZT is said.

[0016] For example, it is lead oxide (PbO). After impressing electric field to a piezo electric crystal thin film, the abundance of a foreign matter should just be regulated so that the abundance of a foreign matter may become the range of a request of a residual strain. For example, 2.5×10 to four or less are desirable. Or it is the range where improvement in the piezo-electric effect like the after-mentioned is obtained. After polarization processing of the piezo electric crystal thin film with which a foreign matter exists is carried out, it is clear to become the cause of a residual strain by X diffraction analysis mentioned later. In addition, a residual strain means a strain in case field strength is 0 kv/cm.

[0017] Since there is little migration of the domain of the piezo electric crystal thin film produced by electric-field impression at the time of polarization processing of a piezo electric crystal thin film or actuation according to this invention, there is [whether a residual strain is small and] almost nothing. This means that there are few hysteresis properties over electric-field impression for a piezo electric crystal thin film. Consequently, a distortion-electrical-potential-difference (electric field) property is good, and can offer a piezo electric crystal thin film with a big variation rate.

[0018] The piezoelectric constant d_{31} from which an index is served as, the piezo-electric effect, i.e., displacement-voltage characteristic, of a piezo electric crystal thin film of this invention, is 180 or more pc/N, and becomes possible [obtaining the piezoelectric constant of 1.2 times or more] as compared with the conventional thing.

[0019] When the variation rate of the piezo electric crystal film impresses an electrical potential difference to a piezo electric crystal thin film, it is generated from a gap of the relative position of a metal atom and an oxygen atom. In the grain boundary between domains (between adjacent crystal grain), an opening occurs as a result of migration of a domain. Existence of this opening reduces the withstand voltage of a piezo electric crystal thin film.

[0020] It is checked by this invention person that decreasing a foreign matter makes a residual strain fall. Moreover, in this invention, lessening width of face of the grain boundary in a piezo electric crystal thin film leads to the ability of the grain boundary itself [used as the radical of the opening leading to residual distortion] to be controlled.

[0021] The crystal grain of a piezo electric crystal thin film constitutes the shape of a column to a vertical electrode, and it is desirable that the direction of field bearing of the crystal concerned is field (001) bearing of tetragonal system or field (111) bearing of a rhombohedral system. In addition, it is good also in the field bearing of (100).

[0022] Since crystallization of the piezo electric crystal thin film by the sol gel process or the MOD process takes place from a lower electrode side, when controlling the crystal orientation of a piezo electric crystal thin film, it needs to be devised. For this reason, it is possible to form seed crystal when forming the crystal of a piezo electric crystal thin film on a bottom electrode.

[0023] Seed crystal (source of a crystal) is constituted on the platinum crystal which consists of titanium and constitutes a lower electrode, or its grain boundary. Said piezo electric crystal thin film has the crystal orientation of field bearing as stated above, and is equipped with the column-like particle size of 0.1 micrometers thru/or the 0.5-micrometer crystal structure.

[0024] Furthermore, the crystal of the piezo electric crystal film which grew as a nucleus is suitably formed ranging over two or more crystal grain of a lower electrode in the source of a crystal formed in the grain boundary of a lower electrode. By carrying out like this, the adhesion between a piezo electric crystal thin film and a lower electrode improves.

[0025] Furthermore, other piezo electric crystal thin films of this invention are characterized by becoming more than a value almost equal to the particle size of said lower electrode, or it, when the particle size of said lower electrode is set as a desirable particle size when said piezo electric crystal demonstrates a piezo-electric property, and the particle size of the crystal of said piezo electric crystal grows considering said source of a crystal as a nucleus.

[0026] The ink jet type recording head of this invention is characterized by having a piezo electric crystal thin film as stated above as vibrator. With one operation gestalt, this ink jet type recording head is characterized by coming to have the substrate with which the ink room was formed, the diaphragm with which the piezo electric crystal thin film in flexurally oscillating mode was fixed to the front face while closing one side of the ink room concerned, and the nozzle plate with which nozzle opening for ink regurgitation was formed while closing the field of another side of said ink room, and said piezo electric crystal thin film consisting of a piezo electric crystal thin film as stated above.

[0027] By forming an island-like crystal kind on between [which constitutes a lower electrode] platinum crystal grain, this seed crystal is used as a nucleus, and it grows up in the shape of a column, and has the predetermined field bearing orientation **** crystal structure. When it is going to obtain the orientation of (111), this island-like titanium is not used.

[0028] Furthermore, when the crystal of said lower electrode is set as a desirable particle size when said piezo electric crystal demonstrates a piezo-electric property, and the crystal of said piezo electric crystal grows considering said source of a crystal as a nucleus, the diameter of crystal grain of said piezo electric crystal can be carried out beyond a value almost equal to the particle size of a lower electrode. That is, since the crystal of a piezo electric crystal thin film can have the structure over two or more lower electrode crystals, it becomes possible to have the particle size exceeding the particle size of a lower electrode. Moreover, by forming the source of a crystal in the grain boundary which cannot receive effect in the stacking tendency of a lower electrode crystal easily, the crystal of a piezo electric crystal thin film can grow as a nucleus, can have this source of a crystal, and the stacking tendency of a piezo electric crystal thin film crystal can be made into the target thing.

[0029] Furthermore, this invention is characterized by the residual distortion of said piezo electric crystal thin film being 2.5×10 to four or less in the piezo electric crystal thin film equipped with the piezo electric crystal thin film it was made to be distorted by impressing electric field. A piezoelectric constant is 150 or more pC/N preferably. Furthermore, this invention is characterized by being the actuator which used these piezo electric crystal thin films as a vibration source.

[0030]

[Embodiment of the Invention] Next, the gestalt of operation concerning this invention is explained with reference to a drawing. In addition, the gestalt of this operation explains the case where the PZT film is formed as piezo electric crystal film. Drawing 1 is the mimetic diagram showing the configuration of the piezo electric crystal component concerning this invention. As shown in

drawing 1 , this piezo electric crystal thin film is equipped with the up electrode 16 formed on a silicon substrate 11, the silicon oxide 12 formed on the silicon substrate 11, the lower electrode 14 formed on silicon oxide the titanite-acid-ized film (Ti/TiO₂/Ti) 13 formed 12 top and the titanite-acid-ized film 13, the PZT film 15 formed on the lower electrode 14, and the PZT film 15, and is constituted. This titanite-acid-ized film is for improving the adhesion of a lower electrode and a PZT thin film. A vertical electrode consists of platinum, for example, respectively.

[0031] The PZT film 15 consists of the polycrystalline substance, and as the grain boundary of this crystal grain shows drawing 14 and drawing 15 , it exists in the direction which extends to the flat surface of the vertical section electrodes 14 and 16 in an abbreviation perpendicular direction and the direction of thickness of a piezo electric crystal thin film. That is, the columnar structure is accomplished like the after-mentioned [the crystal grain of PZT].

[0032] Orientation of the crystal structure of this PZT film 15 is mainly carried out to the crystal face of which field bearing as stated above.

[0033] here — “the amount of preferred orientation” — for example, the wide angle XRD — when the reflectivity of the field bearing (XYZ) side of the PZT film is expressed with I (XYZ) by law, it is defined as being what is expressed as $I(XYZ)/[I(100) + I(110) + I(111)]$.

[0034] That to which this PZT film 15 uses binary system as a principal component, and the thing which uses as a principal component three-component system which added the third component to this binary system are used suitably. What has the presentation expressed with the chemical formula of $Pb(Zr_xTi_{1-x})O_3 + YPbO$ (being here $0.40 \leq x \leq 0.6$, $0 \leq Y \leq 0.3$) as a desirable example of binary system PZT is mentioned.

[0035] Moreover, as a desirable example of three-component system PZT, what has the presentation expressed with the chemical formula shown in the following which added the third component is mentioned to PZT of said binary system.

[0036] $PbTi_aZr_b(AgBh)_cO_3 + ePbO + (fMgO)_n$ (here, A expresses the trivalent metal chosen from the group which consists of a divalent metal chosen from the group which consists of Mg, Co, Zn, Cd, Mn, and nickel, or Sb, Y, Fe, Sc, Yb, Lu, In and Cr.) Moreover, B expresses the pentavalent metal chosen from the group which consists of Nb, Ta, and Sb, or the metal of 6 ** chosen from the group which consists of W and Te. Moreover, although it is $a+b+c=1$, $0.35 \leq a \leq 0.55$, $0.25 \leq b \leq 0.55$, $0.1 \leq c \leq 0.4$, $0 \leq e \leq 0.3$, $0 \leq f \leq 0.15c$, $g=f/2$, and $n=0$ however, A — a trivalent metal — it is — and B — the metal of 6 ** — not but — moreover, the case where g is 1/3, and h is 2/3, and Mg and B of A are Nb(s) when A is a divalent metal and B is a pentavalent metal — as long as — n expresses 1. As a more desirable example of three-component system, magnesium lead niobate, i.e., A, is Mg, B is Nb, and that 1/whose 3h g is 2/3 is mentioned.

[0037] Furthermore, even if it is any of these binary system PZT and three-component system PZT, in order to improve the piezo-electric property, Ba, Sr, La, Nd, Nb, Ta, Sb, Bi, W, Mo, calcium, etc. of a minute amount may be added. In three-component system, addition of Sr not more than 0.10 mol % and Ba is especially much more desirable to an improvement of a piezo-electric property. Moreover, since addition of Mn not more than 0.10 mol % and nickel improves the degree of sintering in three-component system, it is desirable.

[0038] Next, the manufacture approach of the piezo electric crystal thin film equipped with this structure is explained with reference to a drawing. Drawing 2 (a) thru/or drawing 2 (c) are the sectional views showing the production process of the piezo electric crystal thin film mentioned above. At the process shown in drawing 2 (a), it oxidizes thermally to a silicon substrate 11, and the silicon oxide 12 whose thickness is about 0.3–1.2 micrometers is formed on a silicon substrate 11. Next, thickness forms the titanite-acid-ized film 13 which is 0.01 micrometers thru/or about 0.04 micrometers on silicon oxide 12 by the spatter. Subsequently, the diameter of crystal grain forms the lower electrode 14 which consists of platinum by 0.01 thru/or 0.3 micrometers on the titanite-acid-ized film 13 by the spatter at about 0.2–0.8-micrometer thickness.

[0039] Next, at the process shown in drawing 2 (b), titanium is formed in the shape of an island by the spatter on the lower electrode 14 formed at the process shown in drawing 2 (a). Island-like titanium can be formed by making this titanium into 40 thru/or 60Å thickness.

[0040] the crystal structure of the piezo electric crystal thin film which grew considering this titanium as a source of a crystal — or (001) (100) it has the orientation to a field and crystal grain

is set to 0.1 micrometers thru/or 0.5 micrometers. In making crystal system of a PZT thin film into a rhombohedral system (111), it does not use the process which forms island-like titanium.

[0041] This manufacture approach is an approach of carrying out heating baking of a metal alkoxide and the sol which controlled hydrolysis of acetate and carried out stable distribution using alkanolamine or an acetylacetone, and adjusting an inorganic oxide. This manufacture approach consists of each following process.

[0042] a. In the gestalt of membrane formation process book operation of a sol constituent, the constituent for PZT thin film fabrication can distribute the metal alkoxide or the acetate which can form the PZT film which is the metal component of the sol for constituting the PZT film among the 2-n-butoxy ethanol as for example, a main solvent, and can be adjusted. At this time, 2 and 2' imino JIETA Norian (an alkoxide or hydrolysis inhibitor to acetate) is simultaneously put in into a solution.

[0043] In this invention, the presentation of the PZT film mentioned above can be acquired by controlling the presentation of the metal in a sol. That is, let titanium, a zirconium, lead, the alkoxide of each metal component of further others, or acetate be a start raw material.

[0044] Here, there is an advantage that the presentation of the metal component which will constitute the PZT film by the time it considers as the PZT film (piezo electric crystal thin film) eventually is maintained mostly. That is, the presentation of a metal component [in / there are very little metal component and fluctuation especially according to evaporation of a lead component etc. during baking and annealing treatment, therefore / these start raw materials] will be in agreement with the metal presentation in the PZT film obtained eventually. That is, the presentation of a sol is determined according to the piezo electric crystal film (the gestalt of this operation PZT film) which it is going to generate.

[0045] Moreover, in order to obtain the PZT film which does not have lack of a lead component by evaporation of the lead component mentioned above with the gestalt of this operation, 15-mol the thing carried out to an excess to % is preferably more desirable than the amount of which a lead component is required from a stoichiometry in a sol to 20-mol %.

[0046] As for this sol, with the gestalt of this operation, it is desirable to be used as a constituent mixed with the organic high molecular compound. This organic high molecular compound prevents effectively that absorb the residual stress of a thin film at the time of desiccation and baking, and a crack arises in this thin film. If the gel containing this organic macromolecule is specifically used, pore will arise in the gelled thin film which is mentioned later. It is thought that this pore absorbs the residual stress of a thin film in pre annealing and the annealing process which are mentioned further later.

[0047] Here, as an organic high molecular compound used preferably, polyvinyl acetate, hydroxypropylcellulose, a polyethylene glycol, the polyethylene-glycol monomethyl ether, a polypropylene glycol, polyvinyl alcohol, polyacrylic acid, a polyamide, polyamic acid, an acetyl cellulose, its derivative, and those copolymers are mentioned.

[0048] In addition, with the gestalt of this operation, the porosity gel thin film which is 1 micrometer or less in magnitude, and had large distribution can be formed by adding a hydroxy pro PUROI cellulose for the porosity gel thin film which has much about 0.05-micrometer pores by adding polyvinyl acetate.

[0049] With the gestalt of this operation, a with an average molecular weight of about 285 to 800 thing is suitably used as a polyethylene glycol. Moreover, as a polypropylene glycol, a with an average molecular weight of about 300 to 800 thing is used suitably.

[0050] By the manufacture approach concerning the gestalt of this operation, this sol constituent is first applied on the lower electrode 14 (refer to drawing 2 (b)) which is going to form the PZT film 15. Especially the method of application at this time is not limited, but the approach usually performed, for example, a spin coat, (1500 revolutions per minute), a DIP coat, a roll coat, a bar coat, etc. can perform it. Moreover, it can also apply by flexographic printing, screen-stencil, offset printing, etc.

[0051] Moreover, when the process after it is taken into consideration, as for the thickness of the film per [which is formed of said spreading] layer, it is desirable to control so that the thickness of the porosity gel thin film formed in the gelation process mentioned later is set to 0.1 thru/or 0.3

micrometers, and it is good to be more preferably referred to as about 0.15 micrometers.

[0052] Next, the applied sol constituent is heated at air drying or the temperature (for example, 180-degree Centigrade 10 minutes) of 200 degrees C or less. Here, said sol constituent can be further applied on this film dried (heating), and thickness can also be thickened. In this case, as for the film used as a substrate, it is desirable to dry at the temperature of 80 degrees C or more.

[0053] b. Calcinate the film obtained at the gelation process of the film which consists of a sol constituent, next the membrane formation process of a sol constituent mentioned above, and form the porosity gel thin film which consists of an amorphous metallic oxide which does not contain the residual organic substance substantially. Baking is sufficient temperature to gel the film of a sol constituent and remove the organic substance out of the film, and is performed by [sufficient] carrying out time amount heating.

[0054] It is desirable to make burning temperature into 300–500 degrees C with the gestalt of this operation, and it is still more desirable to make it 380–420 degrees C. Although it changes with temperature and the formats of a furnace to be used, when a cleaning furnace is used for example, about 10 – 120 minutes of firing time are desirable, and it is more desirable to consider as about 15 – 60 minutes. Moreover, when a hot plate is used, about 1 – 60 minutes is desirable, and it is still more desirable to consider as about 5 – 30 minutes. Of the above process, a porosity gel thin film is formed on the lower electrode 14.

[0055] c. Carry out heating baking of the porosity gel thin film obtained at the pre annealing process, next the process b mentioned above, and change this film into the film which consists of a metal oxide film of a crystalline substance. What is necessary is not to perform baking until a perovskite mold crystal occupies most during a crystal, and just to terminate it, when a gel thin film crystallizes to homogeneity although carried out at temperature required in order to change a porosity gel thin film into the film which consists of a metallic oxide of a crystalline substance. With the gestalt of this operation, as a burning temperature, the range of 500–800 degrees C is desirable, and it is more desirable to calcinate in the range which is 550–750 degrees C. Although it changes with burning temperature and the formats of a furnace to be used, when using an annealing furnace, for example, about 0.1 – 5 hours of firing time are desirable, and it is more desirable. [of about 0.5 – 2 hours] Moreover, when a RTA (Rapid Thermal Annealing) furnace is used, about 0.1 – 10 minutes is desirable, and about 1 – 5 minutes is more desirable. Here, in RTA, heating for 1 minute was performed Centigrade 600-degree 5-minute + Centigrade 725 degrees in an oxygen ambient atmosphere.

[0056] Moreover, with the gestalt of this operation, this pre annealing process can be divided into two steps, and can be carried out. As a first stage story, annealing can be performed at the temperature of the range of 500–600 degrees C, next, specifically, annealing can be first performed at the temperature of the range of 600–800 degrees C as a second stage story. Furthermore, as a first stage story, annealing can be performed at the temperature of the range of 500–550 degrees C, next annealing can be preferably performed at the temperature of the range of 600–750 degrees C as a second stage story. According to this process, the porosity gel thin film was transformed to the film which consists of a metal oxide film of a crystalline substance.

[0057] d. Change into the film which consists of a metal oxide film according to the pre annealing process of Process C after repeating the processes a and b mentioned above further 3 times a repeat process, next henceforth and carrying out the four-layer laminating of the polycrystal gel thin film.

[0058] In ranking second or (100) (001) forming the piezo electric crystal thin film of orientation, titanium is formed in the shape of an island by the approach as stated above on PZT, and it repeats the processes a, b, and c as stated above further 4 times.

[0059] What is necessary is just to determine suitably the number of laminatings of the cascade screen obtained as a result of this repeat process in consideration of the thickness of the final PZT film 15. Here, it is good that it is 0.15 micrometers of hits much more. In addition, it cannot be overemphasized that it is desirable that it is the thickness which a crack etc. does not generate in degree process (process e) mentioned later.

[0060] At this repeat process, the porosity gel thin film which newly formed the porosity gel thin film and was newly formed on the film formed previously as a result of subsequent pre annealing

turns into film formed previously and film unified substantially.

[0061] Here, a discontinuity layer may be not only when there is no discontinuity layer between the layers by which the laminating was carried out to the film unified substantially but between the layers by which the laminating was carried out unlike the case of the PZT film 15 concerning the gestalt of this operation obtained eventually. And in repeating Processes a and b further, a still newer porosity gel thin film is formed, and this new porosity gel thin film turns into film substantially united with the cascade screen of the crystalline substance obtained above as a result of subsequent pre annealing.

[0062] e. Perovskite mold crystal growth process (final annealing)

Next, annealing is performed on the film obtained at said process d in 800–1000 degrees C still more preferably the burning temperature of 600–1200 degrees C. Although it changes with burning temperature and the formats of a furnace to be used, when an annealing furnace is used for example, about 0.1 – 5 hours of firing time are desirable, and it is more desirable. [of about 0.5 – 2 hours] Moreover, when a RTA furnace is used, about 0.1 – 10 minutes is desirable, and about 0.5 – 3 minutes is more desirable. Here, it set [aforementioned] RTA and this process was performed in 1 minute and 650–degree Centigrade oxygen [5 +900 degree] ambient atmosphere per minute.

[0063] Moreover, with the gestalt of this operation, it can perform dividing this perovskite mold crystal growth process, i.e., annealing, into two steps, and carrying it out. Annealing is performed at the temperature of about 600–800 degrees C, and, specifically, the temperature of 800–1000 degrees C performs annealing on a second stage story on a first stage story. Furthermore, preferably, annealing can be performed at the temperature of about 600–750 degrees C, and the temperature of 800–950 degrees C can perform annealing on a second stage story on a first stage story.

[0064] Of the above actuation, PZT whose thickness the particle size which consists of the column-like polycrystalline substance is 1.2 micrometers in 0.1 micrometers thru/or 0.5 micrometers is formed on the lower electrode 14. Here, the effectiveness which titanium gives about crystallization of PZT is explained. This effectiveness is checked by this invention person using the electron microscope.

[0065] In drawing 1 , island-like titanium is formed of the spatter on the grain boundary of the lower electrode 14. The diameters of crystal grain of a lower electrode are 0.01 thru/or 0.3 micrometers. Since the platinum of using a lower electrode as a columnar crystal with such a diameter of crystal grain is FCC structure, it is easy to become a columnar crystal, and the diameter of crystal grain is possible from the reason for being controllable by the membrane formation rate at the time of a spatter.

[0066] If it is going to form an island-like titanium crystal in the front face of a lower electrode, it will become the inclination for the island-like crystal of titanium to be formed in the grain boundary during the low platinum crystal of the surface energy of platinum. At this time, ranging over two or more titanium crystals, the PZT crystal grain which grows considering titanium as a nucleus reaches, and is formed.

[0067] Drawing 3 is a mimetic diagram in which it is shown like the formation fault of the PZT crystal checked by the electron microscope, (1) is drawing which met in the height direction of a PZT crystal, and (2) is drawing which met in the direction of a path (width of face) of a PZT crystal. Drawing 4 is a actual electron microscope photograph, and the crystal of column-like PZT is formed on Pt electrode. Titanium crystal 14A is formed in the grain boundary of the lower electrode crystal 14.

[0068] If PZT is grown up by using a titanium crystal as a nucleus, the crystal grain will grow so that PZT may straddle two or more platinum crystals of an adjoining lower electrode. Usually, its orientation of 111 is stable, and although production is also easy, if Pt forms the seed crystal of titanium in the grain boundary which cannot be more easily influenced of the orientation of platinum, it can use the crystal of PZT as the columnar crystal of a direction (001) which is not influenced of crystal-face bearing of platinum (100). Furthermore, since the crystal grain of PZT is formed ranging over two or more lower electrodes, it is expected that adhesion with a lower electrode will improve more.

[0069] It is chart drawing of an X-ray diffraction analysis (XRD) when drawing 5 forms the piezo

electric crystal thin film PZT on the lower electrode in which island-like titanium was formed, and drawing 6 is chart drawing when not forming island-like titanium. If drawing 5 is mutually compared with drawing 6, when not forming island-like titanium, orientation (111) becomes strong and the piezo electric crystal constant of the orientation of the PZT film is also 180 pC/N. On the other hand, when island-like titanium is formed, or it is PZT (001) (100), when orientation becomes strong and the rate also increases to orientation (111), a piezoelectric constant also becomes high with 190 pC/N. Here, a piezoelectric constant is that for which it asked from the displacement (distortion)-voltage characteristic, and the piezo-electric effect at the time of impression electric-field 250 kv/cm is shown.

[0070] Furthermore, titanium forms in the shape of an island, and three-layer sequential formation of the PZT layer in which titanium was formed in the shape of an island is carried out, and further, if what carried out four-layer sequential formation of the PZT further is crystallized, titanium is used as a nucleus, and PZT will crystalize like previous statement and it will crystalize according to the diameter of crystal grain and the crystal structure of PZT which other PZT(s) adjoin. The island-like titanium between a PZT layer and a PZT layer is also controlled like previous statement of crystallization of PZT on titanium.

[0071] In addition, it asked for measurement of a piezoelectric strain constant from the distortion-voltage characteristic of the cantilever shown in drawing 9 and drawing 10. That is, a piezoelectric constant (d_{31}) is computed from delta measured since displacement delta was obtained by the degree type and thickness [of Si substrate] H , Young's modulus Y_{Si} and Poisson's ratio ν , Young's modulus Y_{PZT} of the piezo electric crystal film and the free length L of a cantilever, and applied voltage V .

[0072]

$\Delta = d_{31} \cdot V$, and $(Y_{PZT}/Y_{Si}) - (3L^2/H^2) - (1 - \nu_{Si}) / (1 - \nu_{PZT})$ The following relation between epsilon and displacement delta is about distortion, and distortion epsilon can be calculated again.

[0073] t is the thickness of a piezo electric crystal thin film.

[0074] $\epsilon = \{H^2 / (3(1 - \nu_{Si}) t L^2)\} - \Delta$ drawing 7 shows the transmission electron microscope image of the piezo electric crystal thin film obtained here. When this invention person examined the grain boundary (grain boundary) between two adjoining crystals (grain1 and grain2), it was about 5nm or less. There were some which cannot observe the grain boundary mostly. On the other hand, the transparency mold microscope image of the piezo electric crystal thin film created as an example of a comparison of this invention is shown in drawing 8. The film as this example of a comparison added ten-mol superfluous water to one mol of PZT(s) into the sol first, accelerated hydrolysis beyond the need, and it performed at 650 degrees C for 5 minutes, 1 minute performed final annealing temperature at 700 degrees C, and it created it. When this invention person measured the grain boundary of this thing, it had width of face of 7-12nm or more.

[0075] Furthermore, the residual strain to electric-field impression with the piezo electric crystal thin film obtained according to this operation gestalt was measured by making the piezo electric crystal thin film of drawing 8 into the example of a comparison.

[0076] Drawing 9 and drawing 10 are property drawings showing the measurement result when measuring on the conditions of fixing temperature for both residual strain and carrying out increment reduction of the electric field gradually. Drawing 9 is property drawing of the example of a comparison. On the other hand, although drawing 10 was created according to the MOD process, it is a result. as for it, the result of the latter turns out that it is markedly alike compared with the former, and the residual strain is decreasing. When a residual strain falls, the piezo-electric property of the piezo electric crystal thin film of this invention becomes more than d_{31} , and becomes possible [demonstrating one about 1.2 times the piezo-electric strain property of this as compared with the conventional thing]. Measurement of a residual strain was performed using the cantilever. Initial displacement in case an electrical potential difference is zero is equivalent to a residual strain. In the piezo electric crystal thin film with which crystal grain is assembled in the pillar-shaped direction, i.e., a grain boundary, by the thing of bulk with the random direction of a grain boundary of crystal grain, a residual strain becomes large to an almost right-angled thing to a vertical electrode.

[0077] Furthermore, the trial to the foreign matter in the grain boundary of the piezo electric

crystal thin film obtained by this example was performed. This trial was based on the electron ray diffraction pattern obtained according to the conditions of limit visual field diffraction. The white dot shown in drawing 11 and drawing 12 is a PZT crystal. The part shown by drawing 11 and drawing 12 is a part equivalent to the PZT grain boundary, and a PZT crystal presentation is a part for the foreign matter of the presentation from which the part surrounded by ** in this part differs. Drawing 11 is a pattern concerning the example of a comparison, and drawing 12 is a pattern concerning this operation gestalt. The pattern of drawing 12 is understood that there is little abundance of an impurity clearly as compared with the pattern of drawing 11.

[0078] If it returns and explains to drawing 1, after ending the process of drawing 2 (b), it will shift to the process shown in (c). At this process, thickness forms the up electrode 16 which consists of about 0.05–0.2–micrometer platinum by the spatter on the PZT film 15 obtained at the process shown in (b).

[0079] Thus, the piezo electric crystal thin film as shown in drawing 1 was obtained. In addition, it was checked that the surface of discontinuity of the shape of a layer by the laminating which there is no generating of a crack and was mentioned above in the cross section does not exist in the obtained PZT film 15, either.

[0080] Drawing 13 is the sectional view showing one ink reservoir part of the ink jet type recording head which used the piezo electric crystal thin film concerning this invention as a trembler.

[0081] The ink jet type recording head concerning the gestalt 3 of operation The silicon substrate 21 in which the ink reservoir 27 was formed as shown in drawing 13, The diaphragm 22 formed on the silicon substrate 21, and the lower electrode 23 formed in the request location on a diaphragm 22, It is on the lower electrode 23, and it has the piezo electric crystal thin film 24 formed in the location corresponding to the ink reservoir 27, the up electrode 25 formed on the piezo electric crystal thin film 24, and the 2nd substrate 26 joined to the underside of a silicon substrate 21, and is constituted.

[0082] Ink is supplied to the ink reservoir 27 through the ink passage which does not illustrate this ink jet type recording head. Here, if an electrical potential difference is impressed to the piezo electric crystal film 24 through the lower electrode 23 and the up electrode 25, the piezo electric crystal film 24 will deform, it will pressurize in the ink reservoir 27, and a pressure will be applied to ink. It is breathed out by this pressure from the nozzle which ink does not illustrate, and ink jet record is performed with it.

[0083] Since the piezo electric crystal thin film excellent in the piezo–electric property as stated above is used for this ink jet type recording head as vibrator, it can make ink breathe out by the big pressure here. Furthermore, an up electrode shows a piezo–electric high property, when impressing the driver voltage wave used as potential higher than a lower electrode.

[0084] Although titanium was taken up and explained as said source of a crystal, if it cannot be restricted to this, but is the configuration element of the piezo electric crystal film, and it becomes seed crystal and it can alloy with a piezo electric crystal thin film, it will be used not being restricted to titanium. Moreover, although the lower electrode was used as platinum, effectiveness with the same said of iridium with the same FCC structure is acquired.

[0085] Moreover, the creation means of a sol only differs from a sol gel process, and, as for an MOD process as stated above, other conditions are the same as a sol gel process. As for mixing of the sol in an MOD pro cel, a distributed sol does not hydrolyze in the sol liquid after mixing. That is, it is characterized [the object and] by not carrying out the above sol–gel reaction which forms a dehydration polycondensation or a gel network.

[0086] Specifically, one of the alkanolamines and monoethanolamine are chosen as one of the start raw materials of sol liquid as a hydrolysis retardant of metal alkoxide metallurgy group acetate. By work of monoethanolamine, metal alkoxide metallurgy group acetate maintains a uniform distributed condition in sol liquid. Therefore, since the gel network looked at by the sol gel process is not formed, a still more homogeneous crystal can be obtained with a sol gel process. All to the sintering process for obtaining a crystal from the spreading process of a sol is the same as a sol–gel method. Other than the above–mentioned monoethanolamine, diethanolamine, triethanolamine, an acetylacetone, an acetic acid, etc. can be used as a hydrolysis retardant of a sol.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the mimetic diagram showing the configuration of the piezo electric crystal component concerning this invention.

[Drawing 2] It is the sectional view showing the production process of a piezo electric crystal thin film.

[Drawing 3] It is the mimetic diagram in which it is shown like the formation fault of the PZT crystal checked by the electron microscope.

[Drawing 4] It is the actual electron microscope photograph.

[Drawing 5] It is chart drawing of the X-ray diffraction analysis (XRD) at the time of forming the piezo electric crystal thin film PZT on the lower electrode in which island-like titanium was formed.

[Drawing 6] It is chart drawing when not forming island-like titanium.

[Drawing 7] The transmission electron microscope image of the piezo electric crystal thin film obtained here is shown.

[Drawing 8] It is the transparency mold microscope image of the piezo electric crystal thin film created as an example of a comparison of this invention.

[Drawing 9] It is property drawing of the example of a comparison showing the measurement result when measuring on the conditions of fixing temperature for the residual strain of this invention and the example of a comparison, and carrying out increment reduction of the electric field gradually.

[Drawing 10] Temperature is fixed for the residual strain of this invention and the example of a comparison, it is property drawing showing the measurement result when measuring on the conditions of carrying out increment reduction of the electric field gradually, and a result is shown although created according to the MOD process.

[Drawing 11] On the occasion of the trial to the foreign matter in the grain boundary of a piezo electric crystal thin film, it is drawing showing the electron ray diffraction pattern obtained according to the conditions of limit visual field diffraction, and the pattern concerning the example of a comparison is shown.

[Drawing 12] On the occasion of the trial to the foreign matter in the grain boundary of a piezo electric crystal thin film, it is drawing showing the electron ray diffraction pattern obtained according to the conditions of limit visual field diffraction, and the pattern concerning this operation gestalt is shown.

[Drawing 13] It is the sectional view showing one ink reservoir part of the ink jet type recording head which used the piezo electric crystal thin film concerning this invention as a trembler.

[Drawing 14] It is the electron microscope photograph in which the crystal structure of the piezo electric crystal component concerning this invention is shown, and the cross section of the direction of thickness is shown.

[Drawing 15] It is the electron microscope photograph and the crystal structure in the flat surface of a PZT thin film is shown.

[Description of Notations]

11 Silicon Substrate

12 Silicon Oxide

13 Titanic-Acid-ized Film
14 Lower Electrode
15 Up Electrode

[Translation done.]

*** NOTICES ***

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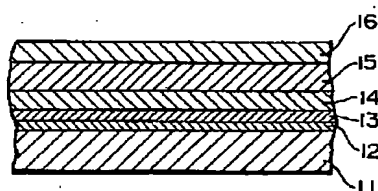
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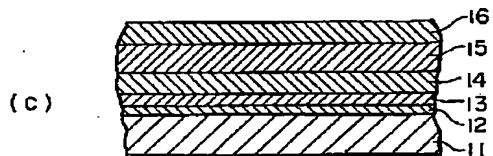
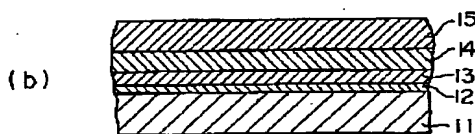
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DRAWINGS

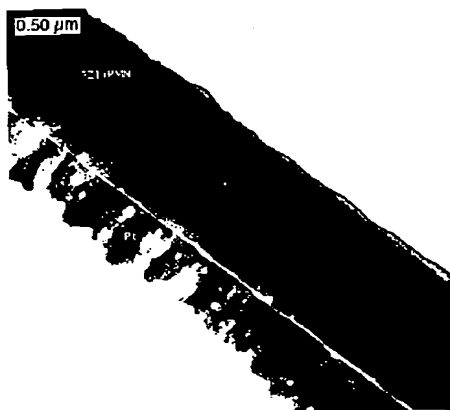
[Drawing 1]



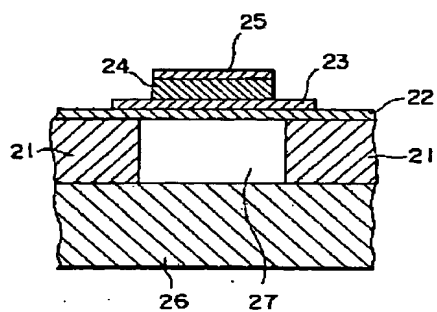
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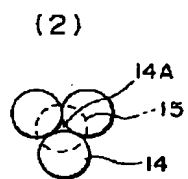
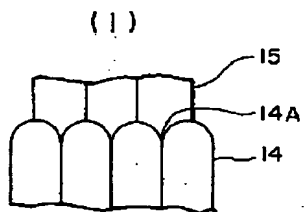
[Drawing 4]



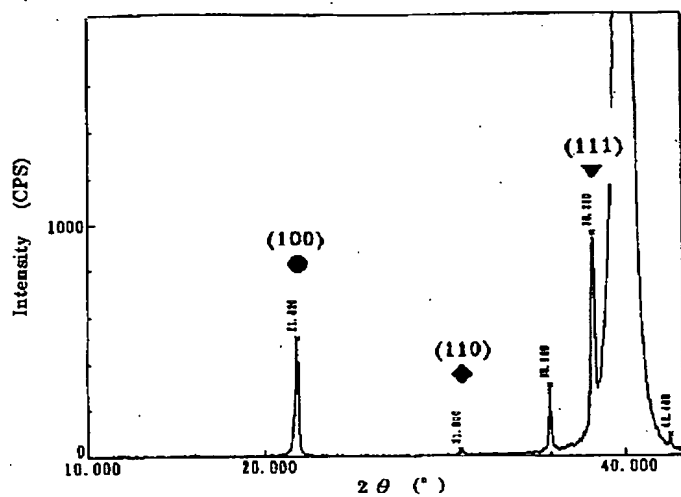
[Drawing 13]



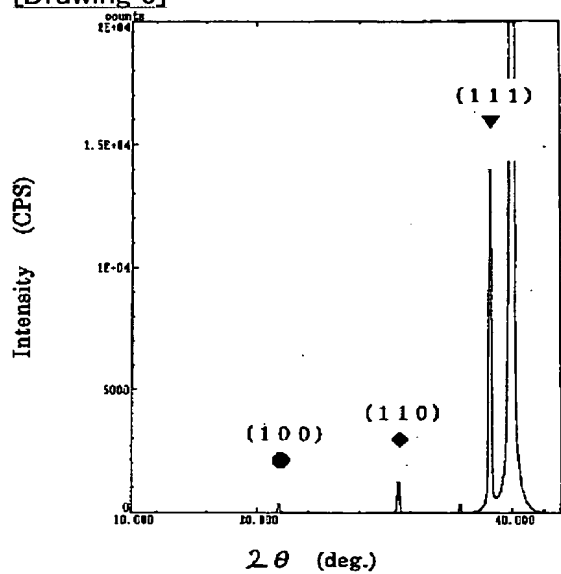
[Drawing 3]



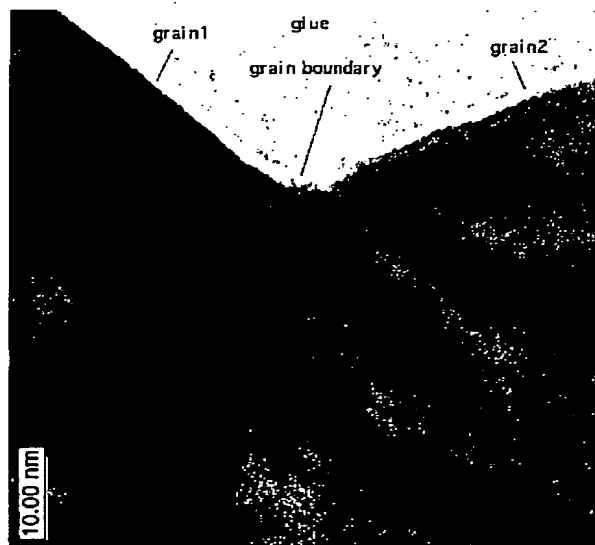
[Drawing 5]



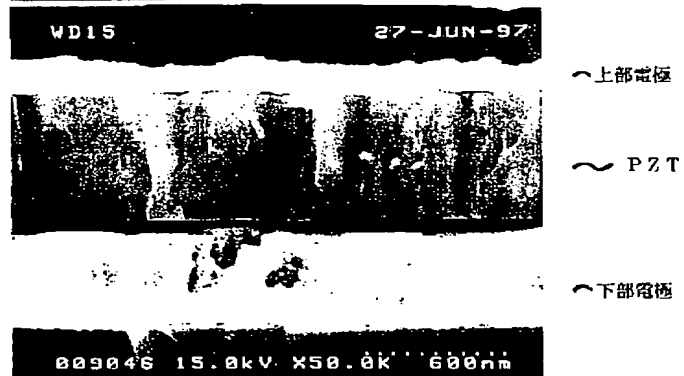
[Drawing 6]



[Drawing 7]



[Drawing 14]



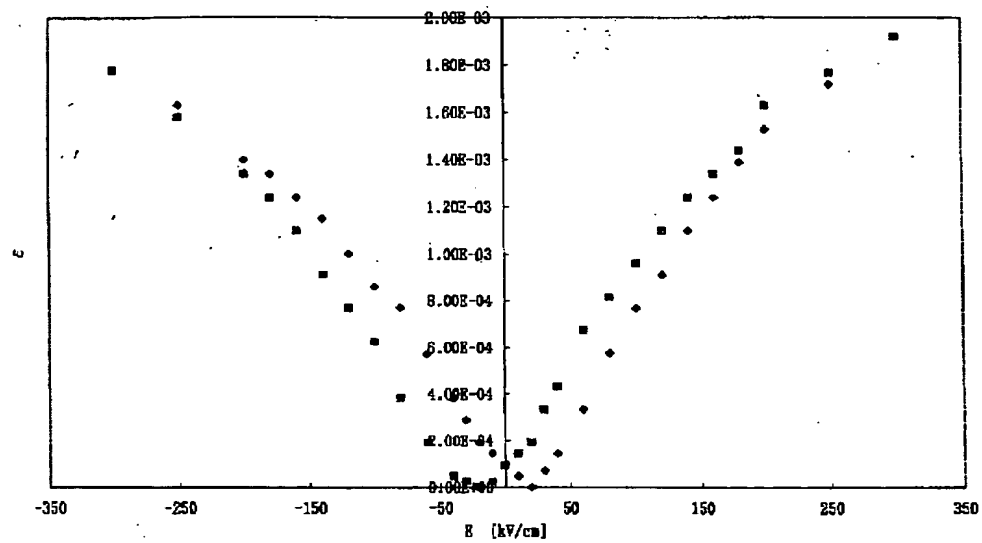
[Drawing 8]

PZT surface ball

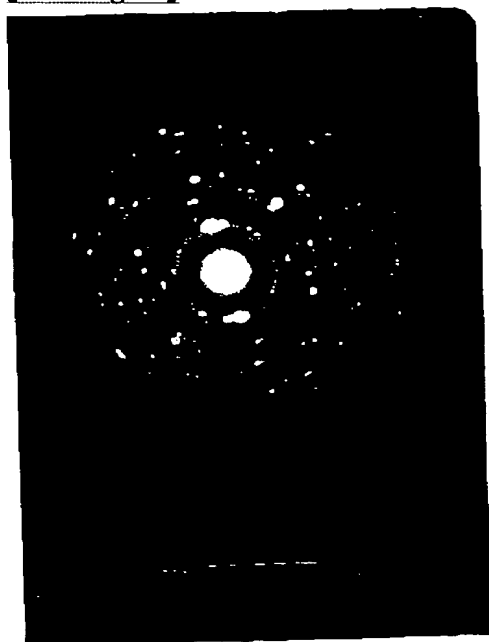


[Drawing 9]

歪み-電場特性



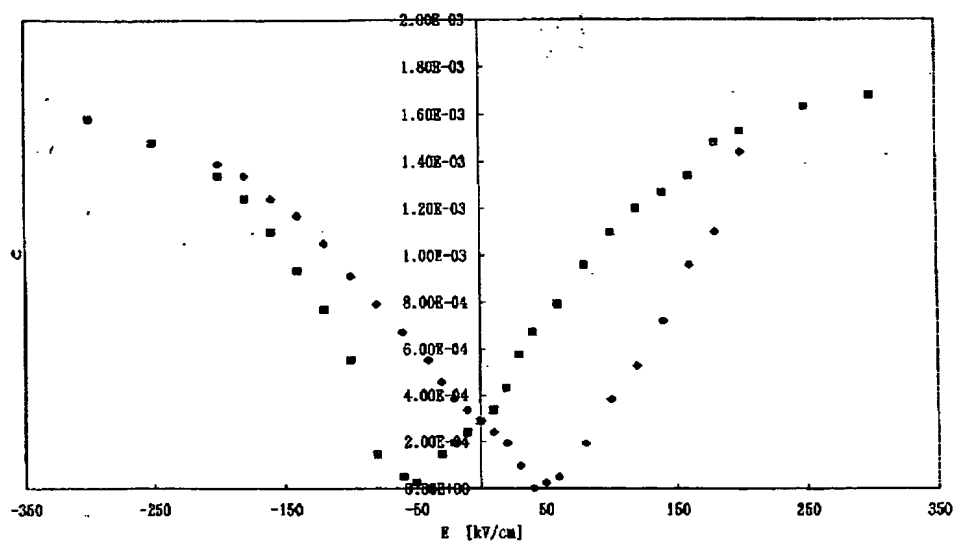
[Drawing 11]



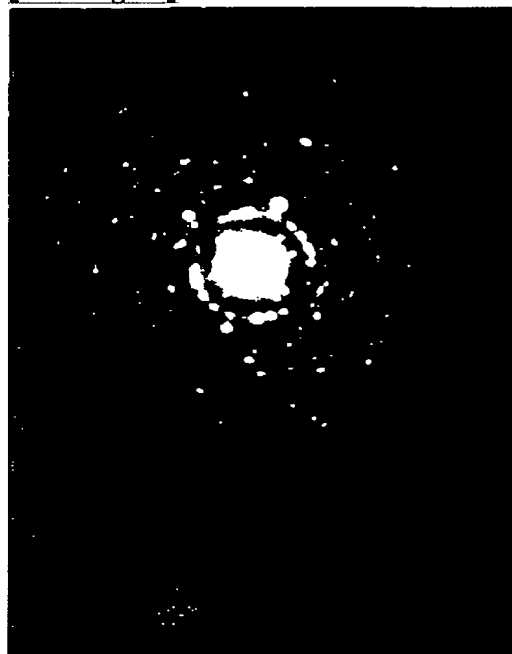
異物あり

[Drawing 10]

歪み-電場特性



[Drawing 12]



異物なし

[Drawing 15]



○PZT表面

[Translation done.]

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(54) 【発明の名称】 圧電体薄膜素子、これを用いたインクジェット式記録ヘッド、インクジェットプリンタ、並びに、圧電体薄膜素子の製造方法

(57) 【要約】

【課題】 圧電体薄膜における残留ひずみの影響を除くことができ、圧電ひずみ特性に優れた機構を提供する。

【解決手段】 圧電体薄膜の結晶粒同士の境界である粒界に、圧電体薄膜素子を分極処理（ポーリング）した後においても、異物が存在しないか、又は異物の存在量が少ないこと。また、粒界の幅が5nm以下であること。また、結晶粒界が隣接する結晶粒の配向とは連続しない、不連続層であること。

【特許請求の範囲】

【請求項 1】 圧電体薄膜と、該圧電体膜を挟んで配置される上部電極と下部電極とを備えた圧電体薄膜素子において、

前記圧電体薄膜を構成する結晶粒と結晶粒との間に、この結晶粒の配向とは連続しない結晶粒界が形成されており、この結晶粒界には前記結晶粒から析出した異物がほぼ存在しない圧電体薄膜素子。

【請求項 2】 さらに、前記結晶粒界のはばが 5 nm 以下である請求項 1 記載の圧電体薄膜素子。

【請求項 3】 圧電体薄膜と、該圧電体膜を挟んで配置される上部電極と下部電極とを備えた圧電体薄膜素子において、前記圧電体薄膜を構成する結晶粒と結晶粒との間に、この結晶粒の配向とは連続しない結晶粒界が形成されており、さらに、この結晶粒界のはばが 5 nm 以下である圧電体薄膜素子。

【請求項 4】 前記結晶粒が前記上下電極に対して柱状を成し、かつ、前記結晶粒界が前記上下電極に対してほぼ垂直方向に存在している請求項 1 乃至 3 のいずれか一項記載の圧電体薄膜素子。

【請求項 5】 前記圧電体薄膜の結晶配向が、(1 1 1) 又は (1 0 0) である請求項 1 乃至 4 のいずれか一項記載の圧電体薄膜素子。

【請求項 6】 前記異物は、前記圧電体薄膜の構成元素からなる所定の化合物であって、この圧電体薄膜が圧電作用を発揮するための組成とは異なる組成を有する化合物である請求項 1 記載の圧電体薄膜素子。

【請求項 7】 前記異物の許容含有量は、前記圧電体薄膜に電界が印加された後に残留ひずみがほぼ残らないことを達成する上で必要な値を上限とするものである請求項 1 記載の圧電体薄膜素子。

【請求項 8】 前記圧電体薄膜が MOD プロセスによって形成されてなる請求項 1 乃至 7 のいずれか一項記載の圧電体薄膜素子。

【請求項 9】 前記結晶粒の面方位の配向が、前記圧電体薄膜の分極軸の配向にほぼ沿っている請求項 1 又は 3 記載の圧電体薄膜素子。

【請求項 10】 前記請求項 1 乃至 9 のいずれか一項記載の圧電体薄膜素子を機械的エネルギー源として用いたアクチュエータ。

【請求項 11】 多結晶体からなる圧電体薄膜を挟んで上部電極と下部電極とを配置する工程を備えた圧電体薄膜素子の製造方法であって、前記圧電体薄膜形成工程を MOD プロセスによって実行し、これにより、請求項 1 又は 3 記載の圧電体薄膜を得ることを特徴とする圧電体薄膜素子の製造方法。

【請求項 12】 請求項 1 ないし請求項 9 のいずれか一項に記載の圧電体薄膜素子を振動子として備えたインクジェット式記録ヘッド。

【請求項 13】 インク室が形成された基板と、当該イ

ンク室の一方を封止すると共に、表面にたわみ振動モードの圧電体薄膜素子が固定された振動板と、前記インク室の他方の面を封止すると共に、インク吐出用のノズル口が形成されたノズル板と、を備えてなるインクジェット式記録ヘッドであって、前記圧電体薄膜素子が、請求項 1 乃至請求項 9 のいずれか一項に記載の圧電体薄膜素子からなるインクジェット式記録ヘッド。

【請求項 14】 請求項 12 又は 13 記載のインクジェット記録ヘッドを備えたインクジェットプリンタ。

10 【請求項 15】 電界を印加することによって歪むようにした圧電体薄膜を備えた圧電体薄膜素子において、前記圧電体薄膜の残留歪みが、 2.5×10^{-4} 以下である圧電体薄膜素子。

【請求項 16】 圧電定数が 150 pC/N 以上の請求項 15 記載の圧電体薄膜素子。

【請求項 17】 請求項 15 又は 16 記載の圧電体薄膜素子を振動源として利用した、アクチュエータ。

【発明の詳細な説明】

【0001】

20 【発明の属する技術分野】本発明は圧電体薄膜素子、その製造方法に関する。本発明はさらに、この圧電体素子を用いたインクジェット記録ヘッド及びこれを用いたインクジェットプリンタに関する。詳しくは、本発明は、残留ひずみを極力低減させた、新規な圧電体薄膜素子の改良に関する。

【0002】

30 【従来の技術】圧電体薄膜素子を用いたアクチュエータは、電気的エネルギーを機械的エネルギーに変換し、またはその逆を行うものであって、圧力センサ、温度センサ、インクジェット式記録ヘッド等に用いられる。このインクジェット式記録ヘッドでは、圧電体薄膜素子をインク吐出の駆動源となる振動子として用いている。

【0003】この圧電体薄膜素子は、一般的に、多結晶体からなる圧電体薄膜と、この圧電体薄膜を挟んで配置される上部電極及び下部電極と、を備えた構造を有している。この圧電体薄膜の組成は、一般的に、チタン酸ジルコン酸鉛（以下、「PZT」という）を主成分とする二成分系、または、この二成分系の PZT に第三成分を加えた三成分系とされている。

40 【0004】これらの組成の圧電体薄膜は、例えば、スパッタ法、ゾルゲル法、MOD プロセス (Metal organic decomposition process)、レーザアブレーション法及び CVD 法等により形成される。これらの例として、二成分系 PZT を用いた強誘電体が、“Applied Physics Letters, 1991, Vol.58, No.11, pages 1161-1163”に記載されている。また、特開平 6-40035 号公報や、“Journal of The American Ceramic Society, 1973, Vol.56, No.2, pages 91-96”には、二成分系 PZT を用いた圧電体が開示されている。

50 【0005】圧電体薄膜素子を、例えばインクジェット

式記録ヘッドに適用する場合、 $0.4\mu\text{m}\sim 20\mu\text{m}$ 程度の膜厚を備えた圧電体薄膜（PZT膜）が好適である。この圧電体薄膜には高い圧電ひずみ定数が要求されるので、通常、 700°C 以上の温度で熱処理を行い、この圧電体薄膜の結晶粒を成長させることが必要であるとされている。

【0006】

【発明が解決しようとする課題】 $0.5\mu\text{m}$ 以上の膜厚を備えた圧電体薄膜（PZT膜）を形成する場合、高い圧電ひずみ定数を得るために熱処理を行うと、膜内にクラックが発生するという問題がある。

【0007】また、ゾルまたはゲル組成物を塗布して高温で焼成して圧電体薄膜を結晶化させ、これを繰り返すことで、圧電体薄膜の膜厚を厚くする方法が、"Philips J. Res. 47 (1993') pages 263-285" に開示されている。

【0008】この方法によって得られた圧電体薄膜は、層状の積層界面を有し、良好な圧電特性を得ることができないとともに、加工性が悪いという問題がある。また、何度も熱処理を行うと、結晶が無配向になる等の圧電特性の劣化にもつながる。

【0009】ここで、圧電体薄膜は、通常、基板上に形成された下部電極上に形成されるが、この圧電体薄膜を形成する際に行われる熱処理により、基板に反りやひずみが生じるという問題がある。また、下部電極と圧電体薄膜との間に、良好な密着性が得られることも必要である。

【0010】そこで、本発明者らが、圧電体薄膜の圧電歪定数を高めるために種々検討したところ、圧電体薄膜の結晶が所定の結晶方向で、かつ、柱状構造を持ち、さらに、粒径が $0.1\mu\text{m}$ 乃至 $0.5\mu\text{m}$ の結晶構造を持つことが有効であることを見出した（特願平9-288757号）。

【0011】しかしながら、さらに本発明者らが検討したところ、次のような問題を発見するに至った。処女状態の圧電体薄膜素子に電界を印加した際、これを取り除いても残留ひずみや分極ひずみが圧電体薄膜素子に発生し、良好な圧電歪み特性（変位特性）を得ることが出来ない。すなわち、圧電体薄膜に電界が加わり、これを分極させると、圧電体薄膜を形成する圧電体のドメイン（結晶粒）は分極軸を電界の方向に合わせるように移動する。すると、粒子同士の粒界に空洞が発生してこれが残留ひずみの原因になると思われる。

【0012】そこで、本発明はこの課題を解決するために、圧電体薄膜における残留ひずみの影響を除くことができ、圧電ひずみ特性に優れた機構を提供することを目的とする。

【0013】

【課題を解決するための手段】本発明者がこのような目的を達成することができる圧電体薄膜について種々検討

した結果、次のような特性を備える圧電体薄膜を見出すに至った。

【0014】圧電体薄膜の結晶粒同士の境界である粒界に、圧電体薄膜素子を分極処理（ポーリング）した後においても、異物が存在しないか、又は異物の存在量が少ないこと。また、粒界の幅が 5nm 以下であること。また、結晶粒界が隣接する結晶粒の配向とは連続しない、不連続層であること。

【0015】本発明者の知見によれば、このような構造は、ゾルゲル法の中でも、既述のMODプロセスを圧電体薄膜の製造に利用することによって好適に達成される。異物とは、PZTを構成する元素から形成される化合物であるが、その組成がPZTとは異なるものを云う。

【0016】例えば、酸化鉛（ PbO ）である。圧電体薄膜素子に電界を印加した後での異物の存在量は、残留ひずみが所望の範囲になるように異物の存在量が規制されれば良い。例えば、 2.5×10^{-4} 以下が好ましい。あるいは、後述のような圧電効果の向上が得られるような範囲である。異物が存在する圧電体薄膜が分極処理された後、残留ひずみの原因になることは、後述するX回析分析によって明らかである。なお、残留ひずみとは電界強度が 0 kV/cm のときのひずみをいう。

【0017】本発明によれば、圧電体薄膜素子の分極処理時又は駆動時の電界印加によって生じる、圧電体薄膜のドメインの移動が少ないので、残留ひずみが小さいか殆ど無い。これは圧電体薄膜素子にとって電界印加に対する履歴特性が少ないことを意味する。その結果、歪み-電圧（電場）特性が良好で、大きな変位を持つ圧電体薄膜素子を提供することができる。

【0018】本発明の圧電体薄膜素子の圧電効果、すなわち、変位-電圧特性は指標となる圧電定数 d_{31} が 180 pC/N 以上であり、従来のものに比較して、1.2倍以上の圧電定数を得ることが可能となる。

【0019】圧電体膜の変位は、圧電体薄膜素子に電圧を印加した際に、金属原子と酸素原子の相対位置のずれから発生する。ドメインの移動の結果、ドメイン間（隣り合う結晶粒間）の粒界には空隙が発生する。この空隙の存在は圧電体薄膜の耐電圧を低下させる。

【0020】異物を減少させることが残留ひずみを低下させることになることは、本発明者によって確認されている。また、本発明において、圧電体薄膜における結晶粒界の幅を少なくすることは、残留歪みの原因となる空隙の基となる結晶粒界そのものを抑制できることに繋がる。

【0021】圧電体薄膜の結晶粒は、上下電極に対して柱状を成し、かつ、当該結晶の面方位方向が、正方晶系の（001）面方位又は菱面体晶系の（111）面方位であることが好ましい。その他、（100）の面方位でも良い。

【0022】ゾルゲル法又はMODプロセスによる圧電体薄膜の結晶化は下部電極側から起こるため、圧電体薄膜素子の結晶配向を制御する上で工夫が必要である。このために、下電極上に圧電体薄膜の結晶を形成する上での種結晶を形成することが考えられる。

【0023】種結晶（結晶源）はチタンから構成されており、かつ下部電極を構成するプラチナ結晶の上或いはその結晶粒界上に構成される。前記圧電体薄膜は既述の面方位の結晶配向を持ち、柱状の粒径0.1 μm 乃至0.5 μm の結晶構造を備える。

【0024】さらに、好適には、下部電極の結晶粒界に形成された結晶源を核として成長した圧電体膜の結晶が下部電極の複数の結晶粒に跨って形成される。こうすることにより、圧電体薄膜と下部電極との間の密着性が向上される。

【0025】さらに、本発明の他の圧電体薄膜素子は、前記下部電極の粒径を前記圧電体が圧電特性を発揮する上で好ましい粒径に設定し、前記圧電体の結晶の粒径が前記結晶源を核として成長することにより、前記下部電極の粒径にほぼ等しい値かそれ以上になることを特徴とするものである。

【0026】本発明のインクジェット式記録ヘッドは、既述の圧電体薄膜素子を振動子として備えたことを特徴とする。一つの実施形態では、このインクジェット式記録ヘッドは、インク室が形成された基板と、当該インク室の一方を封止すると共に、表面にたわみ振動モードの圧電体薄膜素子が固定された振動板と、前記インク室の他方の面を封止すると共に、インク吐出用のノズル口が形成されたノズル板と、を備えてなり、前記圧電体薄膜素子が既述の圧電体薄膜素子からなることを特徴とする。

【0027】下部電極を構成するプラチナ結晶粒間上に島状の結晶種を形成することにより、この種結晶を核にして柱状に成長し、かつ所定の面方位配向持つ結晶構造が備えられる。（111）の配向を得ようとするときには、この島状チタンを用いない。

【0028】さらに、前記下部電極の結晶を前記圧電体が圧電特性を発揮する上で好ましい粒径に設定し、前記圧電体の結晶が前記結晶源を核として成長することにより、前記圧電体の結晶粒径を下部電極の粒径にほぼ等しい値以上にすることができる。すなわち、圧電体薄膜の結晶が、複数の下部電極結晶に跨った構造を持つことができるために、下部電極の粒径を越える粒径を持つことが可能となる。また、下部電極結晶の配向性に影響を受け難い粒界に結晶源を形成することにより、圧電体薄膜の結晶がこの結晶源を核として成長し、もって圧電体薄膜結晶の配向性を目的のものにすることができる。

【0029】さらに、本発明は、電界を印加することによって歪むようにした圧電体薄膜を備えた圧電体薄膜素子において、前記圧電体薄膜の残留歪みが、 2.5×1

0^{-4} 以下であることを特徴とする。圧電定数は、好ましくは150 pC/N以上である。さらに、本発明は、これらの圧電体薄膜素子を振動源として利用した、アクチュエータであることを特徴とする。

【0030】

【発明の実施の形態】次に、本発明に係る実施の形態について図面を参照して説明する。なお、本実施の形態では、圧電体膜としてPZT膜を形成した場合について説明する。図1は本発明に係わる圧電体素子の構成を示す模式図である。図1に示すように、この圧電体薄膜素子は、シリコン基板11と、シリコン基板11上に形成されたシリコン酸化膜12と、シリコン酸化膜12上形成されたチタン酸化膜（Ti/TiO₂/Ti等）13と、チタン酸化膜13上に形成された下部電極14と、下部電極14上に形成されたPZT膜15と、PZT膜15上に形成された上部電極16を、備えて構成されている。このチタン酸化膜は、下部電極とPZT薄膜との密着性を向上するためのものである。上下電極は、それぞれ例えば、プラチナから構成される。

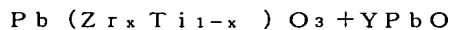
【0031】PZT膜15は多結晶体からなり、この結晶粒の粒界が図14、図15に示すように、上下部電極14及び16の平面に対して略垂直方向、圧電体薄膜の膜厚方向に延びる方向に存在している。すなわち、PZTの結晶粒が後述のように柱状構造を成している。

【0032】このPZT膜15の結晶構造は、既述の何れかの面方位の結晶面に主に配向している。

【0033】ここで、「配向度」とは、例えば、広角XRD法にてPZT膜の面方位（XYZ）面の反射強度をI（XYZ）で表した時に、

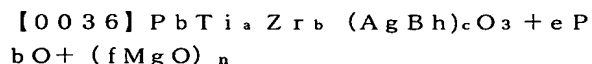
$$I(XYZ)/\{I(100)+I(110)+I(111)\}$$
と表わされるものであると定義する。

【0034】このPZT膜15は、二成分系を主成分とするもの、この二成分系に第三成分を加えた三成分系を主成分とするものが好適に用いられる。二成分系PZTの好ましい具体例としては、



（ここで、 $0.40 \leq x \leq 0.6$ 、 $0 \leq Y \leq 0.3$ ）の化学式で表わされる組成を有するものが挙げられる。

【0035】また、三成分系PZTの好ましい具体例としては、前記二成分系のPZTに、例えば、第三成分を添加した以下に示す化学式で表わされる組成を有するものが挙げられる。



（ここで、Aは、Mg、Co、Zn、Cd、Mn及びNiからなる群から選択される2価の金属またはSb、Y、Fe、Sc、Yb、Lu、In及びCrからなる群から選択される3価の金属を表す。また、Bは、Nb、Ta及びSbからなる群から選択される5価の金属、またはW及びTeからなる群から選択される6価の金属を

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表す。また、 $a+b+c=1$ 、 $0.35 \leq a \leq 0.55$ 、 $0.25 \leq b \leq 0.55$ 、 $0.1 \leq c \leq 0.4$ 、 $0 \leq e \leq 0.3$ 、 $0 \leq f \leq 0.15$ 、 $g=f=1/2$ 、 $n=0$ であるが、但し、Aが3価の金属であり、かつBが6価の金属でなく、また、Aが2価の金属であり、かつBが5価の金属である場合、 g は $1/3$ であり、 h は $2/3$ であり、また、AはMg、BがNbの場合に限り、 n は1を表す。) 三成分系のより好ましい具体例としては、マグネシウムニオブ酸鉛、すなわちAがMgであり、BがNbであり、 g が $1/3$ 、 h が $2/3$ であるものが挙げられる。

【0037】さらに、これら二成分系PZT及び三成分系PZTのいずれであっても、その圧電特性を改善するために、微量のBa, Sr, La, Nd, Nb, Ta, Sb, Bi, W, Mo及びCa等が添加されてもよい。とりわけ、三成分系では、0.10モル%以下のSr, Baの添加が圧電特性の改善に一層好ましい。また、三成分系では、0.10モル%以下のMn, Niの添加が、その焼結性を改善するので好ましい。

【0038】次に、この構造を備えた圧電体薄膜素子の製造方法について図面を参照して説明する。図2(a)ないし図2(c)は、前述した圧電体薄膜素子の製造工程を示す断面図である。図2(a)に示す工程では、シリコン基板11に熱酸化を行い、シリコン基板11上に、膜厚が0.3~1.2 μ m程度のシリコン酸化膜12を形成する。次に、スパッタ法により、シリコン酸化膜12上に、膜厚が0.01 μ m乃至0.04 μ m程度のチタン酸化膜13を形成する。次いで、スパッタ法により、チタン酸化膜13上に、プラチナからなる下部電極14を、結晶粒径が0.01乃至0.3 μ mで、0.2~0.8 μ m程度の膜厚で形成する。

【0039】次に、図2(b)に示す工程では、図2(a)に示す工程で形成した下部電極14上に、チタンをスパッタ法により島状に形成する。このチタンを、例えば、40乃至60オングストロームの膜厚にすることにより島状チタンが形成可能である。

【0040】このチタンを結晶源として成長した圧電体薄膜の結晶構造は、(001)又は(100)面への配向を有し、かつ、結晶粒が0.1 μ m乃至0.5 μ mになる。PZT薄膜の結晶系を菱面体晶系(111)にする場合には、島状チタンを形成する工程を使用しない。

【0041】この製造方法は、アルコールアミン、或いはアセチルアセトン等を用いて、金属アルコキシド、酢酸塩の加水分解を抑制して安定分散したゾルを加熱焼成して無機酸化物を調整する方法である。この製造方法は次の各工程からなる。

【0042】a. ゾル組成物の成膜工程

本実施の形態において、PZT薄膜製造用の組成物は、PZT膜を構成するためのゾルの金属成分である、PZT膜を形成可能な金属のアルコキシドまたはアセテート

を、例えば、主溶媒としての2-n-ブトキシエタノール中分散させて調整することができる。このとき、2,2'-イミノジエタノール(アルコキシド又はアセテートに対する加水分解抑制剤)を溶液中に同時に入れる。

【0043】本発明においては、ゾル中の金属の組成を制御することで、前述したPZT膜の組成を得ることができる。すなわち、チタン、ジルコニウム、鉛、さらには他の金属成分それぞれのアルコキシドまたはアセテートを出発原料とする。

【0044】ここでは、最終的にPZT膜(圧電体薄膜)とされるまでに、PZT膜を構成する金属成分の組成がほぼ維持されるという利点がある。すなわち、焼成およびアニール処理中に金属成分、とりわけ鉛成分の蒸発等による変動が極めて少なく、したがって、これらの出発原料における金属成分の組成は、最終的に得られるPZT膜中の金属組成と一致することになる。つまり、ゾルの組成は生成しようとする圧電体膜(本実施の形態ではPZT膜)に応じて決定される。

【0045】また、本実施の形態では、前述した鉛成分の蒸発により鉛成分の不足のないPZT膜を得るため、ゾルにおいて鉛成分を化学量論から要求される量よりも20モル%まで好ましくは15モル%まで過剰にすることが好ましい。

【0046】本実施の形態では、このゾルは有機高分子化合物と混合された組成物として用いられるのが好ましい。この有機高分子化合物は、乾燥及び焼成時に薄膜の残留応力を吸収して、この薄膜にクラックが生じることを有効に防止する。具体的には、この有機高分子を含むゲルを用いると、後述するゲル化された薄膜に細孔が生じる。この細孔が、さらに後述するプレアニール及びアニール工程において薄膜の残留応力を吸収するものと考えられる。

【0047】ここで、好ましく用いられる有機高分子化合物としては、ポリ酢酸ビニル、ヒドロキシプロピルセルロース、ポリエチレングリコール、ポリエチレングリコールモノメチルエーテル、ポリプロピレングリコール、ポリビニルアルコール、ポリアクリル酸、ポリアミド、ポリアミク酸、アセチルセルロース及びその誘導体、ならびにそれらの共重合体が挙げられる。

【0048】なお、本実施の形態では、ポリ酢酸ビニルを添加することで、0.05 μ m程度の細孔を多数有する多孔質ゲル薄膜を、ヒドロキシプロピルセルロースを添加することで、1 μ m以下の大きさでかつ広い分布を持った多孔質ゲル薄膜を形成することができる。

【0049】本実施の形態では、ポリエチレングリコールとして、平均分子量285~800程度のものが好適に用いられる。また、ポリプロピレングリコールとしては、平均分子量300~800程度のものが好適に用いられる。

【0050】本実施の形態に係る製造方法では、先ず、

このゾル組成物を、PZT膜15を形成しようとする下部電極14（図2(b)参照）上に塗布する。この時の塗布方法は特に限定されず、通常行われている方法、例えば、スピンコート（1500回転/分）、ディップコート、ロールコート、バーコート等によって行うことができる。また、フレキソ印刷、スクリーン印刷、オフセット印刷等によって塗布することもできる。

【0051】また、前記塗布により形成される一層あたりの膜の厚さは、それ以降の工程を考慮すると、後述するゲル化工程において形成される多孔質ゲル薄膜の厚さが0.1乃至0.3 μm となるように制御することが望ましく、より好ましくは0.15 μm 程度とすることがよい。

【0052】次に、塗布されたゾル組成物を自然乾燥、または200℃以下の温度（例えば、摂氏180度10分）で加熱する。ここで、この乾燥（加熱）された膜上に、前記ゾル組成物をさらに塗布して膜厚を厚くすることもできる。この場合は、下地となる膜は、80℃以上の温度で乾燥されることが望ましい。

【0053】b. ゾル組成物からなる膜のゲル化工程
次に、前述したゾル組成物の成膜工程で得た膜を焼成し、残留有機物を実質的に含まない非晶質の金属酸化物からなる多孔質ゲル薄膜を形成する。焼成は、ゾル組成物の膜をゲル化し、かつ膜中から有機物を除去するのに十分な温度で、十分な時間加熱することによって行う。

【0054】本実施の形態では、焼成温度を300～500℃にすることが好ましく、380～420℃にすることがさらに好ましい。焼成時間は、温度及び使用する炉の形式によって変化するが、例えば、脱脂炉を用いた場合には、10～120分程度が好ましく、15～60分程度とすることがより好ましい。また、ホットプレートを用いた場合には、1～60分程度が好ましく、5～30分程度とすることがさらに好ましい。以上の工程によって、下部電極14上に多孔質ゲル薄膜が形成される。

【0055】c. プレアニール工程

次に、前述した工程bで得た多孔質ゲル薄膜を加熱焼成し、この膜を結晶質の金属酸化膜からなる膜に変換する。焼成は、多孔質ゲル薄膜を結晶質の金属酸化物からなる膜に変換するために必要な温度で行うが、結晶中にペロブスカイト型結晶が大部分を占めるまで行う必要はなく、ゲル薄膜が均一に結晶化した時点で終了させればよい。本実施の形態では、焼成温度として500～800℃の範囲が好ましく、550～750℃の範囲で焼成することが、より好ましい。焼成時間は、焼成温度及び使用する炉の形式によって変化するが、例えばアニール炉を使用する場合は、0.1～5時間程度が好ましく、0.5～2時間程度がより好ましい。また、RTA（Rapid Thermal Annealing）炉を用いた場合、0.1～10分程度が好ましく、1～5分程度がより好ましい。こ

では、RTAにおいて酸素雰囲気中摂氏600度5分+摂氏725度1分の加熱を行った。

【0056】また、本実施の形態では、このプレアニール工程を二段階に分けて実施することができる。具体的には、まず、第一段階として、500～600℃の範囲の温度でアニールを行い、次に、第二段階として、600～800℃の範囲の温度でアニールを行うことができる。また、さらに好ましくは、第一段階として、500～550℃の範囲の温度でアニールを行い、次に、第二段階として、600～750℃の範囲の温度でアニールを行うことができる。この工程によって、多孔質ゲル薄膜を結晶質の金属酸化膜からなる膜に変換させた。

【0057】d. 繰り返し工程

次に、以後、前述した工程a、bをさらに3回繰り返し、多結晶ゲル薄膜を4層積層した後、工程Cのプレアニール工程により金属酸化膜からなる膜に変換する。

【0058】次いで、（100）又は（001）配向の圧電体薄膜を形成する場合には、チタンをPZT上に既述の方法によって島状に形成し、既述の工程a、b及びcをさらに4回繰り返す。

【0059】この繰り返し工程の結果得られる積層膜の積層数は、最終的なPZT膜15の膜厚を考慮して適宜決定すればよい。ここでは、一層当たり0.15 μm であることが良い。なお、後述する次工程（工程e）においてクラック等が発生しない膜厚であることが好ましいことは言うまでもない。

【0060】この繰り返し工程では、先に形成した膜上に新たに多孔質ゲル薄膜を形成し、その後のプレアニールの結果、新たに形成された多孔質ゲル薄膜は、先に形成された膜と実質的に一体化された膜となる。

【0061】ここで、実質的に一体化された膜とは、積層された層間に不連続層がない場合のみならず、本実施の形態に係る最終的に得られるPZT膜15の場合と異なり、積層された層間に不連続層があってもよい。そして、さらに工程a、bを繰り返す場合には、さらに新たな多孔質ゲル薄膜が形成され、その後のプレアニールの結果、この新たな多孔質ゲル薄膜は、前記で得た結晶質の積層膜と実質的に一体化された膜となる。

【0062】e. ペロブスカイト型結晶成長工程（ファイナルアニール）

次に、前記工程dで得た膜に、焼成温度600～1200℃、さらに好ましくは800～1000℃の範囲でアニールを行う。焼成時間は、焼成温度や、使用する炉の形式によって変化するが、例えば、アニール炉を用いた場合、0.1～5時間程度が好ましく、0.5～2時間程度がより好ましい。また、RTA炉を用いた場合には、0.1～10分程度が好ましく、0.5～3分程度がより好ましい。ここでは、前記RTAにおいて、摂氏650度5分+900度1分、酸素雰囲気中で本工程を行

【0063】また、本実施の形態では、このペロブスカイト型結晶成長工程、すなわち、アニールを二段階に分けて実施するのができる。具体的には、第一段階では、600～800℃程度の温度でアニールを行い、第二段階では、800～1000℃の温度でアニールを行う。また、さらに好ましくは、第一段階では、600～750℃程度の温度でアニールを行い、第二段階では、800～950℃の温度でアニールを行うことができる。

【0064】以上の操作によって、下部電極14上に、柱状の多結晶体からなる、粒径が0.1μm乃至0.5μmで膜厚が1.2μmのPZTが形成される。ここで、チタンがPZTの結晶化について与える効果について説明する。この効果は、本発明者によって電子顕微鏡を用いて確認されている。

【0065】図1において、下部電極14の粒界上には、島状のチタンがスパッタ法によって形成されている。下部電極の結晶粒径は0.01乃至0.3μmである。下部電極をこのような結晶粒径を持った柱状結晶にすることはプラチナがFCC構造であるため、柱状結晶になりやすく、結晶粒径はスパッタ時の成膜速度により制御できるという理由から可能である。

【0066】下部電極の表面に島状のチタン結晶を形成しようとする、プラチナの表面エネルギーの低いプラチナ結晶間の粒界にチタンの島状結晶が形成される傾向となる。このとき、チタンを核として成長するPZT結晶粒は、複数のチタン結晶に跨って及んで形成される。

【0067】図3は、電子顕微鏡によって確認されたPZT結晶の形成過程を示す模式図であり、(1)はPZT結晶の高さ方向に沿った図であり、(2)はPZT結晶の径(幅)方向に沿った図である。図4は実際の電子顕微鏡写真であり、Pt電極の上に柱状のPZTの結晶が形成されている。チタン結晶14Aは、下部電極結晶14の粒界に形成されている。

【0068】チタン結晶を核としてPZTを成長させると、PZTは隣接する下部電極の複数の白金結晶に跨るようにその結晶粒が成長する。通常、Ptは111の配向が安定で生産も容易であるが、白金の配向の影響をより受け難い結晶粒界にチタンの種結晶を形成すると、PZTの結晶を白金の結晶面方位の影響を受けない(100)、(001)方向の柱状結晶にすることが可能である。さらに、PZTの結晶粒は複数の下部電極に跨って形成されているので、下部電極との密着性がより向上することが期待される。

【0069】図5は島状チタンを形成した下部電極上に圧電体薄膜PZTを成膜した場合のX線回折解析(XRD)のチャート図であり、図6は島状チタンを形成しない場合のチャート図である。図5と図6とを互いに比較すると、島状チタンを形成しない時には、PZT膜の配向は(111)配向が強くなり、圧電定数も180pC/Nである。一方、島状チタンを形成した場合は、P

ZTの(100)又は(001)配向が強くなってその割合も(111)配向に対して多くなることにより、圧電定数も190pC/Nと高くなる。ここで、圧電定数とは、変位(歪み)ー電圧特性から求めたもので、印加電場250kV/cmのときの圧電効果を示すものである。

【0070】さらに、チタンが島状に形成されたPZT層を3層順次形成し、さらにチタンが島状に形成し、さらにPZTを4層順次形成したものを結晶化させると、チタンを核にしてPZTが既述のように結晶化し、他のPZTも隣接するPZTの結晶粒径や結晶構造に合わせて結晶化する。PZT層とPZT層との間の島状チタンもチタン上のPZTの結晶化を既述のように制御する。

【0071】なお、圧電ひずみ定数の測定は、図9、図10に示すカンチレバーの歪みー電圧特性から求めた。即ち、変位δは次式で得られるから測定されたδ及びSi基板の厚みH、ヤング率YSi、また、ポアソン比ν、圧電体膜のヤング率YPZT、及び、カンチレバーの自由長Lと印加電圧Vとから圧電定数(d31)は算出される。

【0072】

$$\delta = d_{31} \cdot V \cdot (Y_{PZT} / Y_{Si}) \cdot (3L^2 / H^2) \cdot ((1 - \nu_{Si}) / (1 - \nu_{PZT}))$$

また、歪みをεと変位δとの間には、以下の関係があり、歪みεを計算できる。

【0073】tは圧電体薄膜の厚さである。

$$\epsilon = \{H^2 / (3(1 - \nu_{Si})tL^2)\} \cdot \delta$$

図7は、ここで得られた圧電体薄膜の透過型電子顕微鏡像を示すものである。隣接する二つの結晶(grain1とgrain2)との間の結晶粒界(grain boundary)は、本発明者が検討したところ、ほぼ5nm以下であった。結晶粒界をほぼ観察できないものもあった。一方、図8には、本発明の比較例として作成した圧電体薄膜の透過型顕微鏡像を示す。この比較例としての膜は、まずゾル中にPZT1モルに対して10モルの過剰な水を加え加水分解を必要以上に加速し、且つファイナルアニール温度を650℃で5分、700℃で1分で行って作成した。このものの結晶粒界は、本発明者が測定したところ、7～12nm以上の幅を持っていた。

【0075】さらに、図8の圧電体薄膜を比較例として、本実施形態によって得られた圧電体薄膜との電界印加に対する残留ひずみを測定した。

【0076】図9、図10は、両者の残留ひずみを温度を一定、電場を徐々に増加減少させるという条件で測定した時の測定結果を示す特性図である。図9は比較例の特性図である。一方、図10はMODプロセスによって作成したものの結果である。後者の結果は、前者に比べて格段に残留ひずみが減少していることが分かる。残留ひずみが低下することにより、本発明の圧電体薄膜の圧電特性は、d31以上となり、従来のものに比較してほぼ1.2倍の圧電ひずみ特性を発揮することが可能とな

る。残留ひずみの測定は、カンチレバーを用いて行った。電圧が零のときの初期変位が残留ひずみに相当する。結晶粒が柱状方向に揃っている圧電体薄膜、すなわち、結晶粒界が上下電極に対してほぼ直角なものに対して、結晶粒の粒界方向がランダムなバルクのものでは、残留ひずみが大きくなる。

【0077】さらに、本実施例によって得られた圧電体薄膜の粒界における異物に対する試験を行った。この試験は、制限視野回折の条件によって得た電子線回折パターンによった。図11、図12に示す白いドットはPZT結晶である。図11、図12で示す部分は、PZT結晶粒界に相当する部分であり、この部分において△で囲む部分が、PZT結晶組成とは異なる組成の異物分である。図11は、比較例に係わるパターンであり、図12は本実施形態に係わるパターンである。図12のパターンは、図11のパターンに比較して明らかに不純物の存在量が少ないことが分かる。

【0078】図1に戻って説明すると、図2(b)の工程を終了した後(c)に示す工程に移行する。この工程では(b)に示す工程で得たPZT膜15上に、スパッタ法によって、膜厚が、0.05~0.2μm程度のプラチナからなる上部電極16を形成する。

【0079】このようにして、図1に示すような圧電体薄膜素子を得た。なお、得られたPZT膜15には、クラックの発生がなく、また断面には前述した積層による層状の不連続面も存在していないことが確認された。

【0080】図13は、本発明に係る圧電体薄膜素子を振動子として使用したインクジェット式記録ヘッドの一つのインク溜め部分を示す断面図である。

【0081】実施の形態3に係るインクジェット式記録ヘッドは、図13に示すように、インク溜め27が形成されたシリコン基板21と、シリコン基板21上に形成された振動板22と、振動板22上の所望位置に形成された下部電極23と、下部電極23上であって、インク溜め27に対応した位置に形成された圧電体薄膜24と、圧電体薄膜24上に形成された上部電極25と、シリコン基板21の下面に接合された第2の基板26と、を備えて構成されている。

【0082】このインクジェット式記録ヘッドは、図示しないインク流路を介してインク溜め27にインクが供給される。ここで、下部電極23と上部電極25とを介して、圧電体膜24に電圧を印加すると、圧電体膜24が変形してインク溜め27内加圧してインクに圧力を加える。この圧力によって、インクが図示しないノズルから吐出され、インクジェット記録を行う。

【0083】ここで、このインクジェット式記録ヘッドは、既述の圧電特性に優れた圧電体薄膜素子を振動子として用いているため、大きな圧力でインクを吐出させることができる。さらには、上部電極は下部電極よりも高い電位となる駆動電圧波形を印加する時高い圧電特性を

示す。

【0084】前記結晶源として、チタンを取り上げて説明したが、これに限られず圧電体膜の構成元素であってかつ種結晶となり、圧電体薄膜と合金化できるものであれば、チタンに限られず使用される。また、下部電極を白金としたが、同じFCC構造を持つイリジウムでも、同様な効果が得られるものである。

【0085】また、既述のMODプロセスは、ゾルの作成手段がゾルゲル法と異なるだけで、その他の条件はゾルゲル法と同じである。MODプロセスに於けるゾルの調合は、調合後のゾル液中で分散ゾルが加水分解をしない。すなわち、脱水重縮合あるいはゲルネットワークを形成する以上のゾルーゲル反応をさせないことを目的、特徴とする。

【0086】具体的には、ゾル液の出発原料の一つにアルカノールアミンの一つ、モノエタノールアミンを金属アルコキシドや金属酢酸塩の加水分解抑止剤として選択する。モノエタノールアミンの働きによって、金属アルコキシドや金属酢酸塩は、ゾル液中で均一な分散状態を保つ。従って、ゾルゲル法に見られるゲルネットワークを形成しないから、ゾルゲル法により更に均質な結晶を得ることができる。ゾルの塗布工程から結晶を得るための焼結工程までの一切は、ゾルーゲル法と同じである。前述のモノエタノールアミンの他に、ジエタノールアミン、トリエタノールアミン、アセチルアセトン、酢酸等をゾルの加水分解抑止剤として利用できる。

【0087】

【発明の効果】以上説明したように、本発明によれば、残留ひずみが少なく、圧電ひずみ特性に優れた圧電体薄膜素子を得ることが可能である。この圧電体薄膜素子は、電界が印加された際優れた変位を発揮することができるので、これを備えたインクジェット記録ヘッドは、インク吐出量を大きくすることができる。

【図面の簡単な説明】

【図1】本発明に係る圧電体素子の構成を示す模式図である。

【図2】圧電体薄膜素子の製造工程を示す断面図である。

【図3】電子顕微鏡によって確認されたPZT結晶の形成過程を示す模式図である。

【図4】その実際の電子顕微鏡写真である。

【図5】島状チタンを形成した下部電極上に圧電体薄膜PZTを成膜した場合のX線回折解析(XRD)のチャート図である。

【図6】島状チタンを形成しない場合のチャート図である。

【図7】ここで得られた圧電体薄膜の透過型電子顕微鏡像を示すものである。

【図8】本発明の比較例として作成した圧電体薄膜の透過型顕微鏡像である。

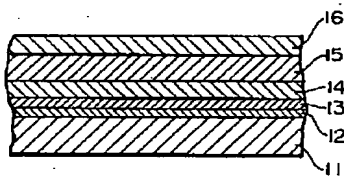
【図 9】本発明と比較例との残留ひずみを温度を一定、電場を徐々に増加減少させるという条件で測定した時の測定結果を示す比較例の特性図である。

【図 10】本発明と比較例との残留ひずみを温度を一定、電場を徐々に増加減少させるという条件で測定した時の測定結果を示す特性図であり、MODプロセスによって作成したものの結果を示す。

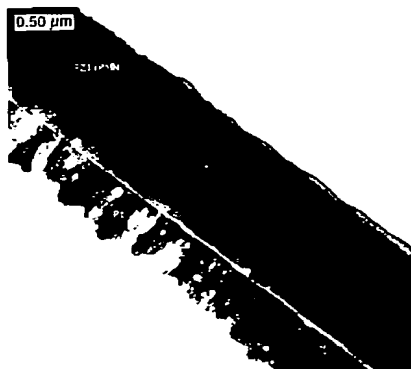
【図 11】圧電体薄膜の粒界における異物に対する試験に際し、制限視野回析の条件によって得た電子線回析パターンを示す図であり、比較例に係わるパターンを示す。

【図 12】圧電体薄膜の粒界における異物に対する試験に際し、制限視野回析の条件によって得た電子線回析パターンを示す図であり、本実施形態に係わるパターンを

【図 1】



【図 4】



示す。

【図 1 3】本発明に係る圧電体薄膜素子を振動子として使用したインクジェット式記録ヘッドの一つのインク溜め部分を示す断面図である。

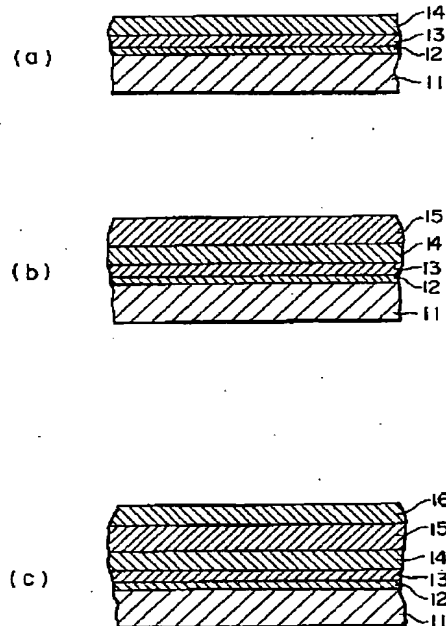
【図 1 4】本発明に係る圧電体素子の結晶構造を示す電子顕微鏡写真であって、膜厚方向の断面を示す。

【図 1 5】その電子顕微鏡写真であって、P Z T 薄膜の平面における結晶構造を示す。

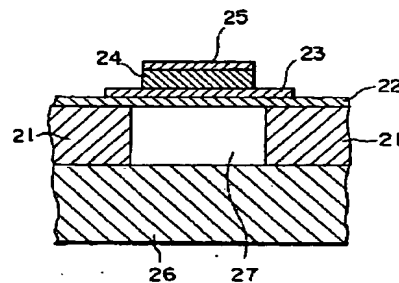
【符号の説明】

- 1 1 シリコン基板
- 1 2 シリコン酸化膜
- 1 3 チタン酸化膜
- 1 4 下部電極
- 1 5 上部電極

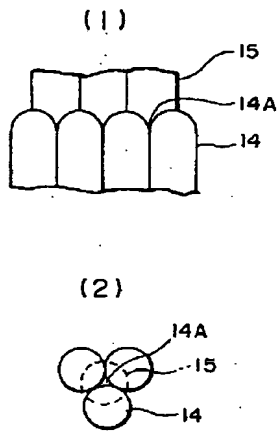
【図 2】



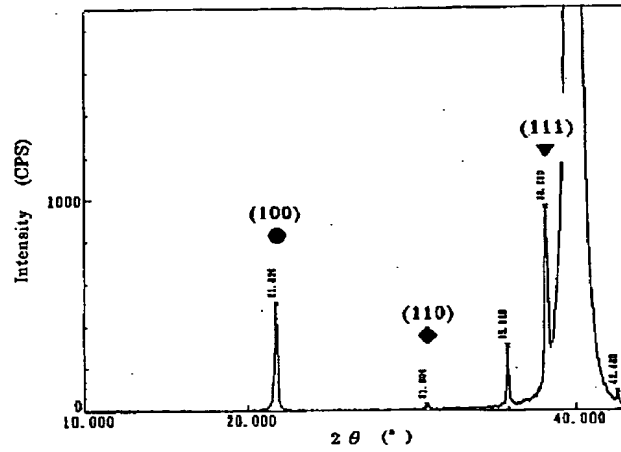
【図 1 3】



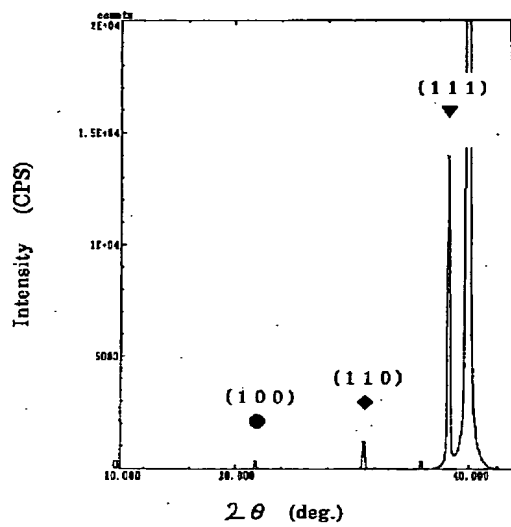
【図 3】



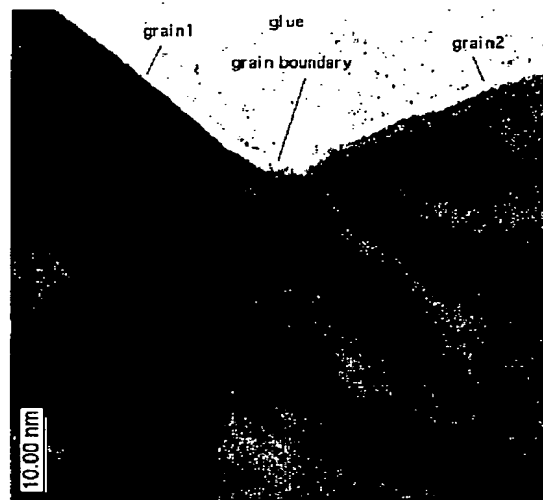
【図 5】



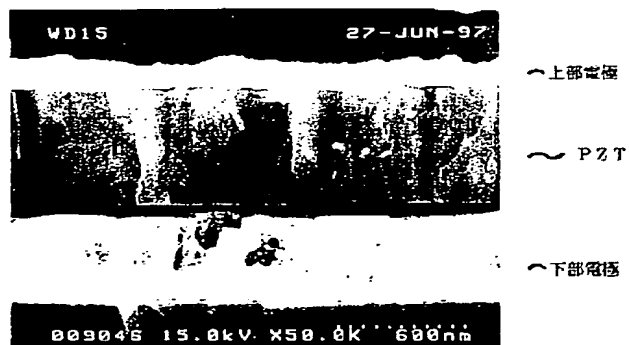
【図 6】



【図 7】



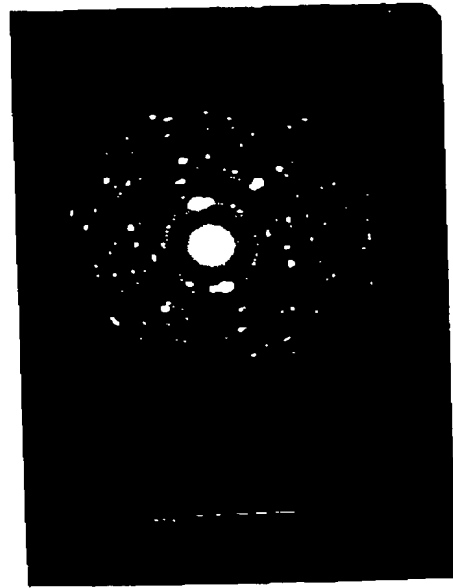
【図 14】



【図 8】

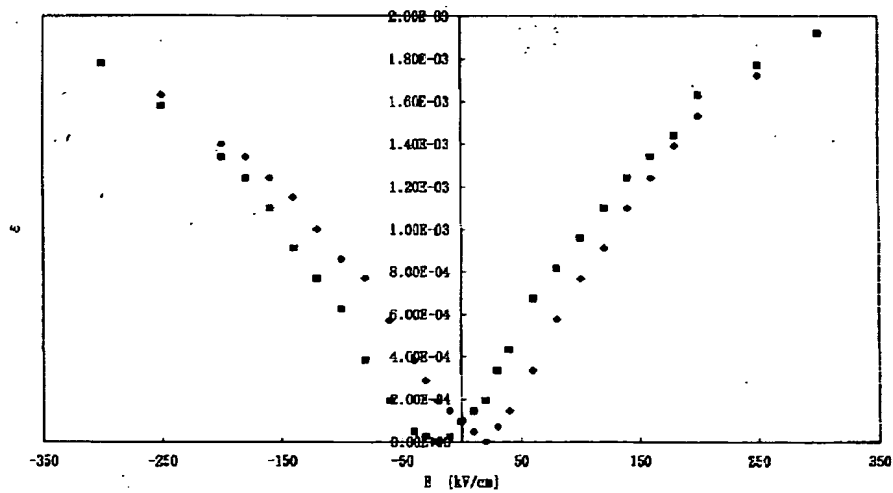


【図 1 1】

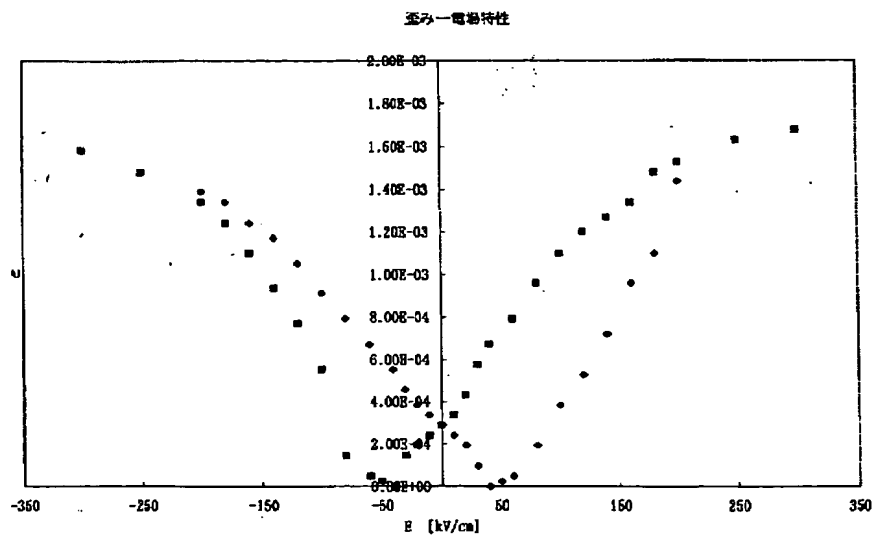


【図 9】

歪み-電場特性



【図 10】

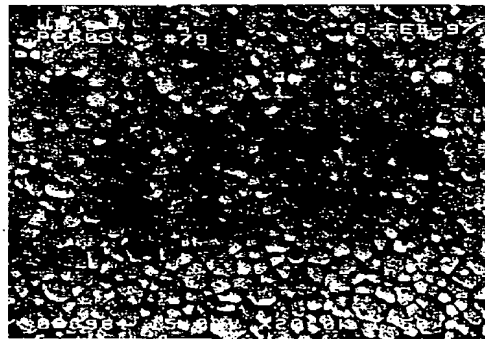


【図 12】



異物なし

【図 15】



PZT表面